PB84-168806

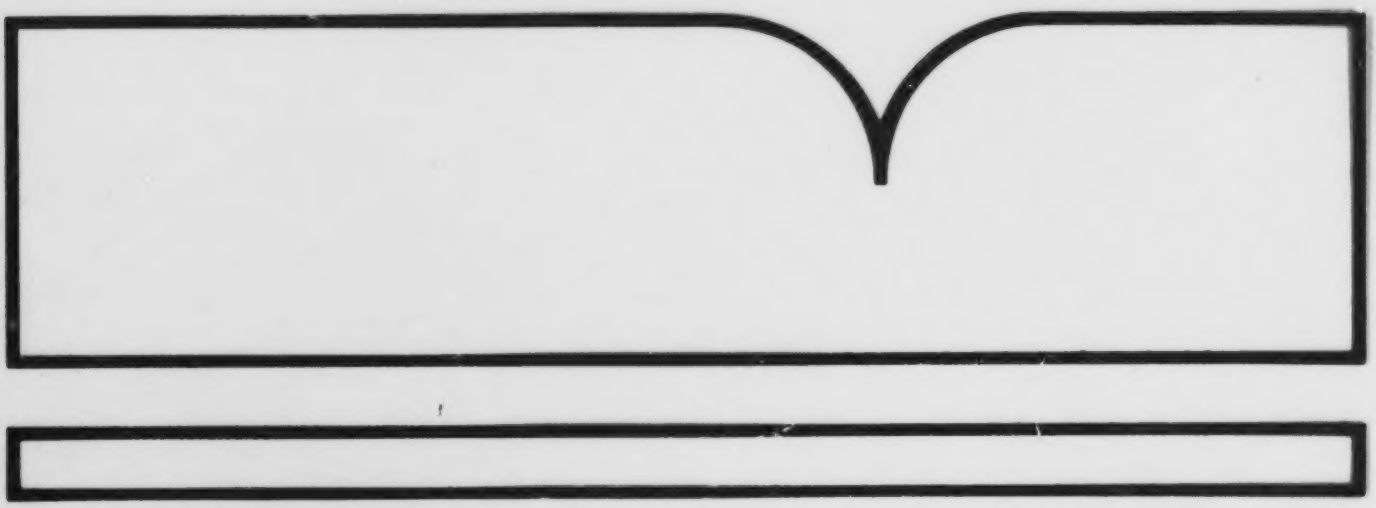
EPA (Environmental Protection Agency) Method Study 23B, Method 501.2 Trihalomethanes by Liquid/Liquid Extraction

Monsanto Research Corp., Dayton, OH

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Mar 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-168806

EPA-600/4-84-021
March 1984

EPA METHOD STUDY 23B, METHOD 501.2, TRIHALOMETHANES BY LIQUID/LIQUID EXTRACTION

by

Beverly J. Warner, Sam C. Cheng, Julie M. Finke,
Charles S. Friedman, Sueann Mitrosky,
Arthur D. Snyder, and Carl R. McMillin
Monsanto Research Corporation
Dayton, Ohio 45407

Contract No. 68-03-2856

Project Officer

Raymond Wesselman
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under contract No. 68-03-2856 to Monsanto Research Corporation. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-84-021	2.
3. RECIPIENT'S ACCESSION NO. PB84 168006	
4. TITLE AND SUBTITLE EPA METHOD STUDY 23B, METHOD 501.2, TRIHALOMETHANES BY LIQUID/LIQUID EXTRACTION	5. REPORT DATE March 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) B.J. Warner, S.C. Cheng, J.M. Finke, C.S. Friedman, S. Mitrosky, A.D. Snyder, and C.R. McMillin	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton, OH 45407	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. 68-03-2856
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/06

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The experimental design and results of a validation study for an analytical method to detect trihalomethanes in water are described herein. This method consisted of a liquid/liquid extraction using pentane and subsequent direct analysis by gas chromatography using an electron capture detector. The six concentrations of spiking solutions contained chloroform, bromodichloromethane, chlorodibromomethane and bromoform. The two waters used in the study were distilled and drinking water, both supplied by the individual laboratories. Statistical analyses and conclusions in this report are based on analytical data obtained by twenty collaborating laboratories. This report was submitted in partial fulfillment of contract 68-03-2856 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers a period from September 1979 to December 1982.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 105
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication, Interlaboratory Study 23B, Method 501.2, "Determination of Trihalomethanes by Liquid/Liquid Extraction, reports the results of EPA's interlaboratory method study for the trihalomethanes: chloroform, bromodichloromethane, chlorodibromomethane, and bromoform.

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this interlaboratory study useful in monitoring and controlling pollution in the environment.

Robert L. Booth, Director

ABSTRACT

The experimental design and results of an interlaboratory study for an analytical method to detect trihalomethanes in water are described herein. In EPA Method 501.2, trihalomethanes are extracted by liquid/liquid extraction using n-pentane (2 mL pentane/10 mL water) and subsequent direct analysis by gas chromatography using an electron capture detector. The six concentrations (three Youden pairs) of spiking solutions used in this study contained chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. The two water types, distilled and drinking water, were supplied by the individual analytical laboratories. Statistical analyses and conclusions are based on analytical data obtained by twenty collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of prestudy samples. The data obtained from the interlaboratory study were analyzed employing a series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which was designed to implement ASTM prodecure D2777. The statistical analyses included tests for the rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

This report was submitted in partial fulfillment of contract No. 68-03-2856 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers a period from September 1979 to December 1982.

CONTENTS

Foreword iii
Abstract v
Tables vii
Acknowledgments ix

1. Introduction 1
2. Conclusions 3
3. Recommendations 6
4. Description of Study 7
   Selection of Participating Laboratories 7
   Phase I - Analysis of Prestudy Conference Samples 8
   Phase II - Prestudy Conference 15
   Phase III - Interlaboratory Method Study 16
5. Statistical Treatment of Data 18
   Rejection of Outliers 18
   Statistical Summaries 23
   Regression Analysis of Basic Statistics 30
   Comparison of Accuracy and Precision Across Water Types 32
6. Results and Discussion 45
   Accuracy 45
   Precision 46
   Effect of Water Type on Accuracy and Precision . . 48
   Comparison of Methods 501.1 and 501.2 50
   Response to Questionnaire 50

References 57

Appendices

A. The analysis of trihalomethanes in drinking water by liquid/liquid extraction, Method 501.2 58

B. Tests of the linearity of Method 501.2 for analysis of trihalomethanes 81

C. Analysis of ampuls used in validation study of Method 501.2 87

D. Raw data 89

TABLES

Number		Page
1	Regression Equations for Accuracy and Precision for Compounds	4
2	Laboratories Participating in EPA Method 501.2 Validation Study	9
3	Procedures for Preparation of Stock Solutions	10
4	Procedures for Preparation of Aqueous Calibration Standards	11
5	Procedures for Spiking Water	12
6	Preconference Results of Method 501.2: Trihalomethanes by Liquid/Liquid Extraction	14
7	Trihalomethane Concentrations in Spiked Solutions	16
8	Youden Laboratory Ranking Procedure for Chloroform Data in Water 2	21
9	Critical Values for Thompson's T-Test When Standard Deviation is Calculated from the Same Samples	22
10	Results of Test for Individual Outliers by the Thompson's T-Test (Chloroform in Water 2)	23
11	Statistical Summary for Chloroform Analyses by Water Type	26
12	Statistical Summary for Bromodichloromethane Analyses by Water Type	27
13	Statistical Summary for Chlorodibromomethane Analyses by Water Type	28
14	Statistical Summary for Bromoform Analyses by Water Type	29

TABLES (continued)

Number		Page
15	Relative Magnitude of Intercepts in the Linear Regression Equations.	33
16	Effect of Water Type on Chloroform Analysis . .	41
17	Effect of Water Type on Bromodichloromethane Analysis.	42
18	Effect of Water Type on Chlorodibromomethane Analysis.	43
19	Effect of Water Type on Bromoform Analysis. . .	44
20	Percent Recovery Statistics (Accuracy).	46
21	Overall Percent Relative Standard Deviation . .	47
22	Single-Analyst Percent Relative Standard Deviation	47
23	Summary of Interlaboratory Precision (% RSD) by Analyte, Water Type, and Concentration Level.	49
24	Summary of Single-Analyst Precision (% RSD-SA) by Analyte, Water Type, and Concentration Level	49
25	Summary of the Tests for Difference Across Water Types	50
26	Regression Equations for Accuracy and Precision for Method 501.2.	51
27	Regression Equations for Accuracy and Precision for Method 501.1.	51
28	Summary of Precision (Percent RSD) by Analyte, Water Type, and Concentration Range (Method 501.1).	52
29	Summary of Precision (Percent RSD-SA) by Analyte, Water Type, and Concentration Range (Method 501.1).	52
30	Laboratory Analytical Conditions.	53

ACKNOWLEDGMENTS

The authors gratefully acknowledge the hard work and cooperation of the staff of the Quality Assurance Branch, EMSL, who assisted in the study. They especially acknowledge the excellent technical assistance, guidance, and understanding of Raymond Wesselman of EMSL. Also acknowledged is the work of Dr. Thomas Bishop at Battelle Columbus Laboratories, Columbus, Ohio, for the statistical analysis of the data under contract No. 68-03-2624.

SECTION 1

INTRODUCTION

The various analytical laboratories of the U.S. Environmental Protection Agency (EPA) gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of these pollution control activities depends upon the reliability of the data provided by the laboratories, particularly when legal action is involved.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Ci), of the EPA develops analytical methods and conducts quality assurance programs for the water laboratories. The quality assurance program of EMSL is designed to maximize the reliability and legal defensibility of all water quality information collected by EPA laboratories. The responsibility for these activities of EMSL is assigned to the Quality Assurance Branch (QAB). One of these activities is to conduct interlaboratory tests of the methods. This study reports the results of the interlaboratory study on Method 501.2 (Study 23B).

The method evaluated in this report was prepared by the EMSL-Cincinnati staff at the request of the Office of Drinking Water, with cooperation from the Technical Support Division, Office of Drinking Water and the Municipal Environmental Research Laboratory. Additional comments and suggestions from the Health Effects Research Laboratory are gratefully acknowledged.

The interlaboratory study of EPA Method 501.2 consisted of three distinct phases. Phase I involved the analysis of the prestudy

samples by 20 participating laboratories. Two samples were analyzed for each of the four trihalomethanes, one in organic-free water and one in drinking water. Both waters were supplied by the individual participating laboratories. The objective of Phase I was to become familiar with the methodology employed and to identify any potential problems associated with the analytical methodology. Accuracy was not as important as being familiar with the methodology. A short report, including the data obtained and any potential problems encountered, was received at the completion of Phase I from each subcontracting laboratory.

Phase II consisted of a prestudy conference held at U.S. Environmental Protection Agency (EPA), Cincinnati, Ohio. Each subcontracting laboratory sent at least one participant to the meeting. The analyst, or principal analyst if more than one analyst was involved, attended this meeting. This meeting, which was held after the data from the prestudy had been evaluated, was designed to examine the results of the prestudy and to discuss any problems encountered in the methodology.

Phase III of the interlaboratory study required the analysis of the study samples. In the case of Method 501.2, the analysis of the four trihalomethanes in both distilled water and drinking water was required at each of six concentrations (three Youden pairs). Again, the participating laboratories supplied the required water samples for these analyses. In addition, the participating laboratories analyzed their distilled and tap water blanks. Each participating laboratory then issued a report containing all data obtained, copies of all chromatograms, and any comments.

The final step in the study was to conduct a statistical analysis of all data obtained. This analysis was conducted by Battelle Memorial Laboratories, Columbus, Ohio, under contract with the U.S. EPA.

SECTION 2

CONCLUSIONS

The objective of this interlaboratory study was to characterize the performance of Method 501.2 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision. Through statistical analyses of 960 analyzed values, estimates of accuracy and precision were made and expressed as regression equations, shown in Table 1.

The accuracy is obtained by comparing the mean recovery to the true values of the concentration. The accuracy, expressed as percent recovery, ranges from 98% to 103% in both water types. The accuracy of the method based on percent recovery is excellent.

The overall standard deviation of the analytical results is an indication of the precision associated with the measurement generated by a group of laboratories. The percent relative standard deviation (% RSD) ranges from 12% to 25% for both water types for the middle and high concentration levels (45 ppb to 174 ppb). The percent relative standard deviation ranges from 18% to 76% for the lowest concentration levels (1.7 ppb to 7.2 ppb) in both water types. The overall standard deviation is very good except at the very low concentration levels.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for single analyst (% RSD-SA) for both water types ranges from 5% to 12% for the middle and high concentrations.

TABLE 1. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR COMPOUNDS

Water type	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
Distilled Water				
Single-analyst precision	SR = 0.06X + 0.76	SR = 0.05X + 0.07	SR = 0.07X + 0.09	SR = 0.07X + 0.24
Overall precision	S = 0.17X + 0.65	S = 0.17X + 0.31	S = 0.16X + 0.47	S = 0.15X + 0.17
Accuracy	X = 1.01C + 0.14	S = 0.98C + 0.02	S = 1.02C + 0.07	X = 1.01C - 2.29
Tap Water				
Single-analyst precision	SR = 0.08X + 1.33	SR = 0.07X + 0.67	SR = 0.07X + 0.30	SR = 0.08X - 0.11
Overall precision	S = 0.26X + 0.60	S = 0.23X + 0.86	S = 0.13X + 0.50	S = 0.16X + 0.11
Accuracy	X = 1.03X - 0.37	X = 1.01C + 0.51	X = 1.00C - 0.05	X = 1.03C - 2.08

X = mean recovery.
C = true value for the concentration.

The lowest concentration levels yield a range of 5% to 81%. The single analyst standard deviation is excellent except at the very low concentration levels.

Method 501.2 performed satisfactorily in the hands of twenty laboratories, who used various instruments and varied conditions. The method is rugged.

The background levels in drinking water were as high as 65 ppb for chloroform and 20 ppb for bromodichloromethane. It is concluded that the low precision is probably due to subtracting a large blank value at low concentration levels.

The comparison on the effect of water types shows a statistically significant difference for bromodichloromethane. However, a practical significant difference does not exist.

SECTION 3

RECOMMENDATIONS

Method 501.2 is recommended for the analysis of trihalomethanes in drinking water. The accuracy is excellent. The overall precision and single-analyst precision are very good except at very low concentrations.

For analytical laboratories located at high altitude, isooctane is the recommended extraction solvent.

Extraction solvents must be checked for contamination. Solvents such as n-hexane and cyclohexane were reported to contain impurities which have the same retention time as chloroform and bromoform. Contamination can come from impurities in the solvent or from impurities being absorbed from the laboratory atmosphere. Recommend analysis for blanks in a daily basis.

SECTION 4

DESCRIPTION OF STUDY

SELECTION OF PARTICIPATING LABORATORIES

In June 1980, as prime contractor, MRC sent requests for quotation (RFQ) to approximately 150 laboratories which had been identified as potential subcontractors for this interlaboratory study. The RFQ contained a Scope of Work, the fixed price allowed for the effort, a description of the projected timing of the required analyses, and a copy of the analytical method. The detailed write-up for Method 501.2 as published by EPA on 15 May 1979 is presented in Appendix A of this report. Interested laboratories were asked to respond to the RFQ with the following information:

- Facilities available at the laboratory, including all instrumentation to be used for the study.
- Previous experience in carrying out the types of analyses specified in the Scope of Work for the compounds of interest.
- Handling procedures for working with hazardous and potentially hazardous chemicals.
- The organization and managerial structure of the laboratory, identifying those personnel involved in managing this study.

- The analyst involved in the analyses to be performed, including his/her experience.

- Quality control/quality assurance procedures and good laboratory practices followed by the laboratory.

Approximately 25 proposals were received in response to the RFQ. The proposals received were ranked, and the twenty most qualified laboratories were selected for participation. Table 2 lists the participating laboratories for the EPA Method 501.2 interlaboratory study. Throughout this report, data provided by these laboratories will be identified only by an anonymous code number.

PHASE I - ANALYSIS OF PRESTUDY CONFERENCE SAMPLES

In November 1980, MRC forwarded to each participating laboratory two sealed glass ampuls containing mixed concentrates of the four trihalomethanes in methanol. Also forwarded were procedures for the preparation of stock solution, procedures for the preparation of aqueous calibration standards, and procedures for spiking the waters with the samples in the ampuls. These recommended procedures are presented in Tables 3, 4, and 5. Some notes on Method 501.2 also were sent to each participating laboratory. The notes included the deletion of Sections 2.3, 2.4, the portion of 3.3 following--"Because of these possible interferences . . . .," and Section 8.3.3. These sections were not appropriate for an interlaboratory study. While the method permits the use of any of three chromatographic columns (Sections 4.10, 4.11, and 4.12), the participating laboratories were required to use the primary column, 3% SP-1000 on 100/120 mesh Supelcoport, described in Section 4.10. MRC had found that a 10-mL screw-cap bottle was preferable for use as the standard storage container (15 mL specified in Section 4.13), and this deviation from the published method was permitted. MRC recommended the use of n-hexane as the extraction solvent because numerous brands of "residue quality"

TABLE 2. LABORATORIES PARTICIPATING IN EPA METHOD 501.2 VALIDATION STUDY

Acurex Corporation
285 Clyde Avenue
Mountain View, CA 94042

Analytics
Division of CBL
Subsidiary of Rohm & Haas Co.
1415 Rhoadmiller
Richmond, VA 23260

Clayton Environmental Consultants, Inc.
25711 Southfield Road
Southfield, MI

Engineering Science, Inc.
Research and Development Laboratory
600 Bancroft Way
Berkeley, CA 94710

Environmental Research Group, Inc.
117 North First
Ann Arbor, MI 48104

ERCO/Energy Research Co., Inc.
185 Alewife Brook Parkway
Cambridge, MA 02138

Global Geochemistry Corp.
6919 Eton Avenue
Canoga Park, CA 91303

Jacobs Laboratories (formerly PJB Laboratories)
373 South Fair Oaks Avenue
Pasadena, CA 91105

Normandeau Associates, Inc. (formerly Texas Instruments, Inc.)
1710 Firman Drive
Richardson, TX 75081

Northrop Services, Inc.
Environmental Services
P.O. Box 437
Little Rock, AR 72203

O'Brien & Gere Engrs., Inc.
Box 4873
1304 Buckley Road
Syracuse, NY 13221

Orlando Laboratories, Inc.
P.O. Box 8008
90 West Jersey Street
Orland, FL 32806

PedCo Environmental, Inc.
11499 Chester Road
Cincinnati, OH 45246

Serco Laboratories
Sanitary Engineering Laboratories, Inc.
1931 West County Road, C2
Roseville, MN 55113

State of New York
Department of Health
Tower Building
The Governor Nelson A. Rockeller Empire State Plaza
Albany, NY 12201

Technical Services, Inc.
103-7 Stockton Street
P.O. Box 52329
Jacksonville, FL 32201

UBTL, Division of University of Utah Research Institute
520 Wakara Way
Salt Lake City, UT 84108

Versar, Inc.
6621 Electronic Drive
Springfield, VA 22151

Weston Designers Consultants
Weston Way
West Chester, PA 19380

Wilson Laboratories
Analytical & Research Chemists and Biologists
528 North Ninth
Salina, KS 67401

TABLE 3. PROCEDURE FOR PREPARATION OF STOCK SOLUTIONS

1. Place about 9.8 mL of methyl alcohol into a ground glass stoppered 10-mL volumetric flask.

2. Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.

3. Weigh the flask to the nearest 0.1 mg.

4. Using a 100-µL syringe, immediately add 2 drops of the reference standard to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5. Dilute to volume, stopper, then mix by inverting the flask several times.

6. Transfer the solution to a dated and labeled 15-mL screw-cap bottle with a Teflon® cap liner.

7. Calculate the concentration in micrograms per microliter from the net gain in weight.

8. Store the solution at 4°C.

   All standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

   Because of the toxicity of the purgeables, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

TABLE 4. PROCEDURE FOR PREPARATION OF AQUEOUS CALIBRATION STANDARDS

To prepare accurate standard solutions, the following precautions must be observed:

- Do not inject more than 20 µL of alcoholic standards into 100 mL of reagent water.
- Use a 25-µL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix aqueous standards by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous standards when stored with a headspace are not stable and should be discarded after one hour.

TABLE 5. PROCEDURE FOR SPIKING WATER

If duplicate analyses are to be performed on one ampul, concurrently perform all of the following steps below in duplicate:

- Fill a 100-mL volumetric flask to volume with reagent water.
- Stablize the ampuls to 20°C.
- Use a 25-µL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Open the ampuls by breaking off the top at the break area on the neck and immediately fill the syringe.
- Rapidly inject 20 µL of the ampul concentrate into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix the sample by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous solutions when stored with a headspace are not stable and should be discarded after one hour.

pentane had shown interfering peaks with the same retention time as chloroform (ref. Section 5.1). MRC also recommended that the organic-free water used in preparation of aqueous calibration standards be obtained fresh each day, because the water tends to pick up chlorinated compounds from laboratory air (ref. Section 5.6.4).

Two preliminary samples were sent to the participating laboratories. One of the samples contained 40 to 50 µg/L of the four trihalomethanes and the other contained approximately 1 µg/L of the four trihalomethanes. The analysis of the high-level sample assured that the method could be properly implemented by the laboratories in the absence of difficulties. The analysis of the low-level sample evaluated any method or detection limit problems under more adverse conditions. The results of these analyses are presented in Table 6.

In Table 6, the data are shown after correction for the blank values of the trihalomethanes in the various laboratories' drinking water. If the value for a compound in the blank was greater than or equal to the value in the sample, ND (not detected) is reported. N-1 statistics were used to calculate the standard deviation where ND was calculated as "0," $<X_i$ was calculated as "X_i," and NA (not analyzed) was ignored in the calculations. The "true value" listed for each individual compound is the calculated value of the final concentration in the drinking water after adding the prescribed 20-µL volume of the concentrated spiking solution (delivered in sealed ampuls) to the prescribed 100-mL volume of drinking water.

Prior to the study conference, MRC analysts conducted a brief test on EPA Method 501.2 to establish calibration curves and to demonstrate linearity of the analytical method. As a result, the linearity for analysis of the trihalomethanes by Method 501.2 was

TABLE 6. PRECONFERENCE RESULTS OF METHOD 501.2: TRIHALOMETHANES BY LIQUID/LIQUID EXTRACTION (µg/L)

Laboratory	Compound							
	Chloroform		Bromodichloromethane		Chlorodibromomethane		Bromoform	
01	48	<0.1	58	1.7	64	1.7	3.8	<1
02	41.7	1.9	54.1	1.5	62	1.5	4.11	1.5
03	37	30	53	7.6	59	3.2	0.9	<0.7
04	38.70	ND[b]	41.37	0.85	75.01	1.63	3.84	0.95
05	29.7	1.4	54.2	1.7	40.8	1.2	3.1	1.0
06	3.7	0.27	4.9	0.1	6.6	0.14	0.4	0.09
07	27.28	ND	45.2	1.80	96	2.4	3.37	2.1
08	98	83	99	7	100	5	12	6
09	46	1.4	55	1.7	70	1.6	4.6	1.2
10	47.4	ND	41.7	10.1	17.9	6	10.9	8
11	27	21	30	22	52	19	ND	ND
12	32	17	52	11	60	7.3	3.7	1.2
13	36.5	2.79	34.2	1.38	50.9	1.91	4.7	1.29
14	45	1	52	12	61	3.0	3.6	<1.7
15[a]								
16	217	63	36	7	33	3	ND	ND
17	49.50	0.84	52.96	0.56	75.18	19.25	0.50	ND
18*	45.2	17.6	34.2	0.80	57.6	10.6	2.61	1.01
19[a]								
20[a]								
True value	40	1.0	40	1.0	51	1.3	50	1.0
Mean	52	14	48	5.5	58	4.9	3.7	1.7
Standard deviation	48	25	19	6.0	25	5.9	3.5	2.2
Range	3.7 - 217	ND - 83	4.9 - 99	0.12 - 22	6.6 - 100	0.14 - 19.25	ND - 10.9	ND - 8

*Reported at prestudy conference and not included in statistics.

[a]No data reported by these laboratories.

[b]Data reported as "not detected" calculated as 0. Data reported as $<X_i$ calculated as X_i.

verified for the range of concentrations from 5 to 200 µg/L used in this study. A discussion of this work and the associated calibration curves that were generated are presented in Appendix B of this report.

PHASE II - PRESTUDY CONFERENCE

After the participating laboratories analyzed the prestudy conference samples, the analysts from the 20 participating laboratories met in Cincinnati, Ohio on 15 January 1981 to discuss the EPA Method 501.2 procedure and potential problems. Potential problems identified at this meeting included the following:

- A large number of laboratories experienced difficulty in attempting to get the trihalomethanes to elute in the time reported in Method 501.2 under the stated conditions. Allowable changes to Method 501.2 that may aid in the analysis included the following:
  - The column I.D. may be changed to 2 mm from 4 mm.
  - The temperature may be increased as necessary.
  - The flow may be changed to accomodate the above changes.
- Most laboratories reported finding relatively high concentrations of varying numbers of the trihalomethanes in their drinking water. This, of course, is to be expected. The detection limits for drinking water for the trihalomethanes will potentially be higher than those in distilled water.
- There appeared to be a universal problem in finding a suitable extraction solvent that contained no chloroform interference.
- The low boiling point of the extracting solvent preferred by the EPA, n-pentane, created a problem for a laboratory situated at a high altitude. Although the extraction solvent was not dictated, for most laboratories, n-pentane was still recommended as the solvent of choice.

PHASE III - INTERLABORATORY METHOD STUDY

Method study samples were sent to participating laboratories in March 1981. The design of the method study was based on Youden's original plan [1] for the collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs instead of in duplicate, and each sample of a pair has slightly different concentrations of the constituents. The analyst is directed to perform a single analysis and report one value for each sample.

Six spiking solutions were made such that three different concentration ranges were each represented by two different solutions (a Youden pair). Solution numbers 1 and 2 had trihalomethanes at low levels of about 2 µg/L. Solution numbers 3 and 4 had concentrations near the drinking water standards of 50 µg/L. Solutions 5 and 6 contained trihalomethanes at levels about three times the intermediate levels. Table 7 shows the calculated trihalomethane concentrations for each spiked solution.

TABLE 7. TRIHALOMETHANE CONCENTRATIONS IN SPIKED SOLUTIONS (µg/L)

Concentration	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
1	1.76	1.76	1.76	5.99
2	2.25	2.25	2.25	7.25
3	45.2	44.8	44.9	45.2
4	55.0	55.0	55.0	55.0
5	131	130	131	130
6	170	170	174	170

Verification of the concentration of the trihalomethanes in the ampuls shipped to the participating laboratories was conducted by both MRC and the Quality Assurance Branch of EPA/EMSL. Method

501.2 was employed by MRC while the direct injection GC-MS technique was used by EPA. The combined data indicated that the ampuls were correctly prepared. The mean recoveries of the participating laboratories also support the verification of the ampuls. Verification results are provided in Appendix C.

Instructions to participating laboratories for the analysis of drinking water and distilled water included the procedures for preparation of stock solutions, calibration standards, and quality control ampuls that had been recommended for the prestudy conference analysis (see Tables 3 through 5). Each laboratory was directed to spike 100 mL of individual drinking water samples from their laboratory with 20 µL of each of the following ampuls and to analyze a drinking water blank:

501.2 Conc. 1	501.2 Conc. 2	501.2 Conc. 3
501.2 Conc. 4	501.2 Conc. 5	501.2 Conc. 6

Each laboratory also was directed to spike individual distilled water samples from their laboratory with 20 µL of each from a set of similarly labeled ampuls, and to analyze a distilled water blank. Forms were provided for reporting the analytical results in µg/L of all samples using the following significant-figure format:

XXX
XX.X
X.XX
0.XX

SECTION 5

STATISTICAL TREATMENT OF DATA

Data obtained from the interlaboratory study were subjected to statistical analyses by the Battelle Columbus Laboratories, Columbus, Ohio, under EPA Contract 68-03-2624. The analyses were performed employing the Interlaboratory Method Validation Study (IMVS) system [2] of computer programs. This system of programs was designed to implement ASTM procedure D2777, "Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water" [3]. The analyses conducted using the IMVS system included tests for the rejection of outliers (both whole laboratories for a water-type and individual data points), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

REJECTION OF OUTLIERS

An outlying observation, or "outlier," is a data point that appears to deviate markedly from other members of the sample in which it occurs. Outlying data points are very commonly encountered during interlaboratory test programs; if they are not removed, they can result in a distortion of the accuracy and precision statistics which characterize the analytical method. These outlying points cannot be removed indiscriminantly, however, because they may represent an extreme manifestation of the random variability inherent in the method.

ASTM procedure E178-80, "Standard Practice for Dealing with Outlying Observations" [4], and ASTM procedure D2777-77 [3] present explicit statistical rules and methods for identification of outliers.

Data from outlying laboratories for a particular water type were rejected employing Youden's laboratory ranking test procedure [3, 5] at the 5% level of significance. Data remaining after the laboratory ranking procedure were subjected to individual outlier tests. After all zero, missing, "less than" and "nondetect" data were rejected as outliers, the average and standard deviation for all remaining data were calculated. The data then were examined for additional outliers employing the two-sided Thompson's T-test for outlier rejection [6]. All data rejected as outliers for this study are identified by an asterisk in the tables of raw data shown in Appendix D.

Youden's Laboratory Ranking Procedure

Using the data for each water type, Youden's laboratory ranking test [3, 5] was performed at the 5% level of significance. The Youden laboratory ranking procedure requires a complete set of data from each laboratory within each water type. Missing data from laboratory i for water type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for water type j and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where β_j and γ_j are fixed parameters which determine the effect of water type j; L_i is the systematic error due to laboratory i, and ε_{ijk} is the random within-laboratory error.

Taking natural logarithms, it follows that

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

which is a linear regression model with dependent variable $\ell n\, X_{ijk}$ and independent variable $\ell n\, C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each water type. The predicted values for $\ell n\, X_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $X_{ijk} = \exp(\ell n\, X_{ijk})$. (For complete details of this procedure, see Reference 2.)

An example of the use of Youden's laboratory ranking procedure is presented in Table 8, where the rankings of the values for chloroform in water 2 are listed for each laboratory and for ampuls 1 through 6. For 20 laboratories and 6 ampuls, the upper and lower critical limits of the sums of the rankings are 104 and 22. If the sum of the rankings of any laboratory equals or exceeds 104, or is equal to or less than 22, that laboratory's data is rejected for all determinations for that analyte (chloroform) in that water (water 2). From Table 8 it is apparent that the data from Laboratories 10, 18, and 20 must be rejected. The estimated missing data were then removed from the data sets.

Test for Individual Outliers

The data remaining after rejection of all zero, missing, "less than" and "nondetect" data were subjected to an individual outlier test based on calculation of Thompson's T-value.

TABLE 8. YOUDEN LABORATORY RANKING PROCEDURE FOR CHLOROFORM DATA IN WATER 2

Laboratory number	Ranking values						Cumulative score
	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6	
1	5	7	12	12	11	12	59
2	11	12	16	14	13.5	10.5	77
3	18.5	19	7	6	7	2	59.5
4	16	16	14	10	12	10.5	78.5
5	9	8	15	13	15	13	73
6	7	5	17	16	18	17	80
7	18.5	10	13	5	2	7	55.5
8	18.5	19	6	20	19	19	101.5
9	14	3	3	2	5	5	32[a]
10	1	2	5	3	3	1	15[a]
11	18.5	17	19	18	13.5	16	102
12	3	19	10	11	10	8	61
13	8	9	4	9	4	4	38
14	12	6	2	7	6	3	36
15	4	4	9	8	9	9	43
16	15	13	18	17	16	14	93
17	6	11	8	15	17	17	75
18	2	1	1	1	1	15	21[a]
19	13	14	11	4	8	6	56
20	10	15	20	19	20	20	104[a]

[a]Laboratories rejected versus upper and lower criteria of 104 and 22.

The criterion for rejection of individual outliers is based on calculation of the t-value [3,6].

In these calculations the mean recovery, $\bar{x}$, is given by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \qquad (3)$$

and the standard deviations, s, is given by

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2} \qquad (4)$$

where x_i = individual analyses
n = number of retained analyses values in the ampul set

Thompson's T is defined by

$$T = \frac{x_e - \bar{x}}{s} \qquad (5)$$

where x_e is the retained x_i value farthest away from the mean ($\bar{x}$) of the set of retained values.

The outlier may be rejected if the value of T calculated exceeds the critical value for T (two-sided test) as presented in Table 11. The 5% significance level was employed. If the extreme value is rejected as an outlier, the test is repeated for the next extreme value among the data until the value being tested is less than the critical T-value.

TABLE 9. CRITICAL VALUES FOR THOMPSON'S T (TWO-SIDE TEST) WHEN STANDARD DEVIATION IS CALCULATED FROM THE SAME SAMPLES

Number of observations, n	5% significance level
6	1.89
7	2.02
8	2.13
9	2.21
10	2.29
11	2.36
12	2.41
13	2.46
14	2.51
15	2.55
16	2.58
17	2.62
18	2.65
19	2.68
20	2.71

TABLE 10. RESULTS OF TEST FOR INDIVIDUAL OUTLIERS BY THE t-TEST (CHLOROFORM IN WATER 2)

Ampul	Lab	Extreme Value x_e	Mean $\bar{x}$	Standard deviation s	Calculated T $\frac{x_e - \bar{x}}{s} = T$	Number of points i	Critical T T_c	Decision
1	12	8.30	1.63	2.12	3.15	13	2.46	Reject
4	9	97.90	56.29	13.78	3.02	16	2.58	Reject
5	7	260.00	139.77	44.20	2.72	17	2.62	Reject

As shown in Table 10 three additional data points are identified as outliers by the Thompson's T-test for the illustrative example of the analyte chloroform in water 2. In summary, of the original 120 data points for chloroform in water 2 (20 laboratories x 6 ampuls), all data points for laboratories 10, 18, and 20 were rejected on the basis of Youden's laboratory ranking procedure (total of 18 points), and three additional data points were found to be outliers based on the Thompson's T-test (for a total of the 21 data points that are identified by an asterisk as outliers in Table 8). These same tests were applied for all other analytes in both waters.

STATISTICAL SUMMARIES

After the outlier rejection tests were performed, the following summary statistics were calculated employing the remaining data for each ampul (single analyte, single concentration, single water matrix):

- Number of retained data points, n
- Mean recovery of retained data, $\bar{X}$
- Accuracy as a percent of relative error, % RE
- Overall absolute standard deviation, S
- Percent relative overall standard deviation, % RSD

- Absolute single-analyst standard deviation, S_r
- Percent relative single-analyst standard deviation, % RSD-SA

All of these statistics, except the single-analyst absolute and relative standard deviations, were calculated using the retained data for each ampul. The basic statistical formulas used for these calculations are given below, where X_1, X_2,..., X_n denote the values for the n retained data points for a given ampul.

Mean Recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

Accuracy as a % Relative Error:

$$\% \text{ RE} = \frac{\bar{X} - \text{true value}}{\text{true value}} \times 100 \qquad (6)$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2} \qquad (4)$$

and

Percent Relative Overall Standard Deviation:

$$\% \text{ RSD} = \frac{S}{\bar{X}} \times 100 \qquad (7)$$

The overall standard deviation, S, indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in a collaborative study. A measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by S_r, is measured by

$$S_r = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2} \qquad (8)$$

where m = number of retained Youden-paired observations
D_i = difference between observations in the i^{th} pair
$\bar{D}$ = average of D_i values

The Youden-pair design employed in this study permits the calculation of this single-analyst precision without making duplicate measurements on the same sample. This helps to avoid the well-intentioned manipulation of data that can occur when laboratories make duplicate analyses.

The percent relative standard deviation for the single-analyst precision is calculated by

$$\% \text{ RSD-SA} = \frac{S_r}{\bar{X}^*} \times 100 \qquad (9)$$

where $\bar{X}^*$ is the average of the two mean recoveries corresponding to the two ampuls defining the particular Youden pair. These summary statistics are presented in Tables 11 through 14 for each of the four trihalomethanes in the two water matrices.

TABLE 11. STATISTICAL SUMMARY FOR CHLOROFORM ANALYSES BY WATER TYPE

	Water 1		Water 2	
Low Youden pair	1	2	1	2
Number of data points	17	18	12	14
True value, ug/L	1.76	2.25	1.76	2.25
Mean recovery	1.53	2.31	1.08	2.54
Accuracy as % rel error	-13.20	2.52	-38.73	13.02
Overall std dev, S	0.82	1.21	0.74	2.12
Overall rel std dev, %	53.95	52.65	68.19	83.31
Single analyst				
Std dev, S_r	0.87		1.47	
Rel dev, $\%_r$	45.49		81.39	
Medium Youden pair	3	4	3	4
Number of data points	18	17	17	15
True value, ug/L	45.20	55.00	45.20	55.00
Mean recovery	45.56	53.83	48.46	53.52
Accuracy as % rel error	0.80	-2.13	7.21	-2.69
Overall std dev, S	8.21	7.73	9.98	8.46
Overall rel std dev, %	18.03	14.36	20.60	15.81
Single analyst				
Std dev, S_r	4.12		6.22	
Rel dev, $\%_r$	8.29		12.19	
High Youden pair	5	6	5	6
Number of data points	18	18	16	17
True value, ug/L	131.00	170.00	131.00	170.00
Mean recovery	131.00	173.17	132.26	167.89
Accuracy as % rel error	0.00	1.86	0.96	-1.24
Overall std dev, S	24.63	29.12	33.39	43.26
Overall rel std dev, %	18.80	16.81	25.24	25.77
Single analyst				
Std dev, S_r	8.29		11.18	
Rel dev, $\%_r$	5.45		7.45	

WATER LEGEND

1 - Distilled water
2 - Tap water

TABLE 12. STATISTICAL SUMMARY FOR BROMODICHLORO-METHANE ANALYSES BY WATER TYPE

	Water 1		Water 2	
Low Youden pair	1	2	1	2
Number of data points	16	16	17	17
True value, ug/L	1.76	2.25	1.76	2.25
Mean recovery	1.76	2.18	2.33	2.71
Accuracy as % rel error	-0.11	-3.31	32.19	20.63
Overall std dev, S	0.62	0.69	1.43	1.44
Overall rel std dev, %	35.54	31.66	61.33	53.24
Single analyst				
Std dev, S_r	0.17		0.85	
Rel dev, $\%_r$	8.74		33.66	
Medium Youden pair	3	4	3	4
Number of data points	17	16	18	17
True value, ug/L	44.80	55.00	44.80	55.00
Mean recovery	48.57	57.91	50.26	56.85
Accuracy as % rel error	8.42	5.28	12.18	3.37
Overall std dev, S	8.21	8.95	12.68	12.26
Overall rel std dev, %	16.90	15.45	25.24	21.57
Single analyst				
Std dev, S_r	2.84		4.22	
Rel dev, $\%_r$	5.33		7.89	
High Youden pair	5	6	5	6
Number of data points	16	16	17	17
True value, ug/L	130.00	170.00	130.00	170.00
Mean recovery	129.68	132.46	144.02	138.11
Accuracy as % rel error	-0.25	-22.08	10.78	-18.76
Overall std dev, S	26.00	24.95	37.19	32.40
Overall rel std dev, %	20.05	18.84	25.82	23.46
Single analyst				
Std dev, S_r	7.00		10.94	
Rel dev, $\%_r$	5.34		7.76	

WATER LEGEND

1 - Distilled water
2 - Tap water

TABLE 13. STATISTICAL SUMMARY FOR CHLORODIBROMOMETHANE ANALYSIS BY WATER TYPE

	Water 1		Water 2	
Low Youden pair	1	2	1	2
Number of data points	18	18	16	16
True value, ug/L	1.76	2.25	1.76	2.25
Mean recovery	1.75	2.21	1.81	2.04
Accuracy as % rel error	-0.51	-1.83	2.59	-9.56
Overall std dev, S	0.77	0.78	0.67	0.85
Overall rel std dev, %	44.13	35.43	36.88	41.90
Single analyst				
Std dev, S_r	0.23		0.43	
Rel dev, $\%_r$	11.83		22.35	
Medium Youden pair	3	4	3	4
Number of data points	18	17	15	15
True value, ug/L	44.90	55.00	44.90	55.00
Mean recovery	45.28	56.61	45.77	56.42
Accuracy as % rel error	0.84	2.92	1.95	2.59
Overall std dev, S	5.74	7.05	6.39	8.10
Overall rel std dev, %	12.67	12.45	13.97	14.36
Single analyst				
Std dev, S_r	4.08		4.72	
Rel dev, $\%_r$	8.01		9.25	
High Youden pair	5	6	5	6
Number of data points	18	17	14	14
True value, ug/L	131.00	174.00	131.00	174.00
Mean recovery	138.19	173.82	131.11	169.00
Accuracy as % rel error	5.49	-0.10	0.08	-2.87
Overall std dev, S	28.75	34.52	17.12	21.39
Overall rel std dev, %	20.80	19.86	13.06	12.66
Single analyst				
Std dev, S_r	10.48		7.36	
Rel dev, $\%_r$	6.72		4.90	

WATER LEGEND

1 - Distilled water
2 - Tap water

TABLE 14. STATISTICAL SUMMARY FOR BROMOFORM ANALYSES BY WATER TYPE

	Water 1		Water 2	
Low Youden pair	1	2	1	2
Number of data points	15	15	12	14
True value, ug/L	5.99	7.25	5.99	7.25
Mean recovery	3.96	4.74	4.60	4.65
Accuracy as % rel error	-33.87	-34.59	-23.25	-35.89
Overall std dev, S	0.86	0.72	0.67	1.01
Overall rel std dev, %	21.63	15.21	14.58	21.77
Single analyst				
Std dev, S_r	0.53		0.23	
Rel dev, $\%_r$	12.24		5.05	
Medium Youden pair	3	4	3	4
Number of data points	17	16	15	15
True value, ug/L	45.20	55.00	45.20	55.00
Mean recovery	45.07	54.43	45.30	54.93
Accuracy as % rel error	-0.29	-1.03	0.22	-0.13
Overall std dev, S	6.93	7.34	7.27	9.13
Overall rel std dev, %	15.37	13.48	16.05	16.62
Single analyst				
Std dev, S_r	3.78		4.97	
Rel dev, $\%_r$	7.59		9.91	
High Youden pair	5	6	5	6
Number of data points	17	17	15	15
True value, ug/L	130.00	170.00	130.00	170.00
Mean recovery	127.56	165.59	131.89	173.07
Accuracy as % rel error	-1.88	-2.60	1.45	1.80
Overall std dev, S	19.60	26.74	20.94	26.16
Overall rel std dev, %	15.37	16.15	15.88	15.11
Single analyst				
Std dev, S_r	9.58		7.60	
Rel dev, $\%_r$	6.53		4.99	

WATER LEGEND

1 - Distilled water
2 - Tap water

REGRESSION ANALYSIS OF BASIC STATISTICS

Systematic relationships frequently exist between the mean recovery statistics and the true concentration levels across ampuls, and between the precision statistics and the mean recovery statistics. Given a plot of precision values versus concentration levels, a smooth curve drawn through the points can show that the precision is found to (1) be constant and not vary with level, (2) vary directly with level in a linear manner, or (3) vary with level in a curvilinear fashion.

In order to derive statements for method accuracy and precision, the basic statistics were regressed assuming linear relationships, fitting the data to a line using weighted least-squares. The weights were chosen to be inversely related to the true concentration in the case of accuracy and inversely related to the mean recovery in the case of precision. The inverse weightings were employed to minimize skewing created by the high Youden-pair data. The results of the regression analyses are discussed below.

Statements of Method Accuracy

The accuracy of Method 501.2 is characterized by comparing the mean recovery of the analyte, $\bar{X}$, to the true concentration level of the compound, C, in the ampul. The IMVS program conducts these calculations via matrix algebra, where weighted least-squares linear regression of $\bar{X}$ versus C is conducted with weights chosen to be inversely related to the square of the true concentration levels (see page 108 of Reference 2 for details). This method is equivalent to that suggested by Britton [7] where the linear regression for $\bar{X}$ versus C is achieved by using the customary least-squares algorithm to fit:

$$\frac{\bar{X}}{C} = a + b\left(\frac{1}{C}\right) \qquad (10)$$

which can then be converted to the desired relationships by multiplying through by C, giving:

$$\bar{X} = aC + b \qquad (11)$$

These equations were presented earlier in Table 1.

If the intercept (b) associated with the fitted line is negligible (i.e., essentially zero), then the slope (a) provides a unique value which represents the percent recovery over all of the concentration levels.

Statements of Method Precision

The precision of Method 501.2 is characterized by comparing the overall and single-analyst standard deviations to the mean recovery, $\bar{X}$. The IMVS program conducts these calculations via matrix algebra, where a weighted least-squares linear regression of S and S_r versus $\bar{X}$ is conducted with weights chosen to be inversely proportional to the square of the mean recovery (see page 108 of Reference 2 for details). This method is equivalent to that suggested by Britton [7] where the linear regressions for S and S_r versus C are achieved by using the customary least-squares procedure to fit the equation:

$$\frac{S}{C} = c + d\left(\frac{1}{C}\right) \qquad (12)$$

In this study, however, the regression was conducted versus $\bar{X}$ as follows:

$$\frac{S}{\bar{X}} = c + d\left(\frac{1}{\bar{X}}\right) \qquad (13)$$

which is then converted by multiplying through by $\bar{X}$ to yield the linear relationships

$$S = a\bar{X} + b \qquad (14)$$

and

$$S_r = c\bar{X} + d \qquad (15)$$

These equations also were presented earlier in Table 1.

If the intercepts, b and d, are negligible, then the slopes, a and c, are good approximations to the overall and single-analyst percent relative standard deviations, respectively. These, in turn, are measures of the method precision.

As a test of the relative magnitudes of the intercept values, average values of S, S_r, and $\bar{X}$ were calculated from the data in Tables 11 through 14 over the three concentration levels reported in this study. Table 15 presents the average values for the statistical quantities and the percentage of these averages represented by the intercept. In most cases (especially for the single-analyst standard deviation statistics), the intercepts cannot be considered to be negligible. This, in turn, questions whether the slopes of the linear regression equations are good approximations of the accuracy and precision of Method 502.2. This problem will be discussed in a later section.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 501.2 depend on the type of water being analyzed. The summary statistics $\bar{X}$, S, and S_r are calculated separately for each concentration level within each water type. They can be compared across

TABLE 15. RELATIVE MAGNITUDE OF INTERCEPTS IN THE LINEAR REGRESSION EQUATIONS

	Chloroform		Bromodichloromethane		Chlorodibromomethane		Bromoform	
	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value
Distilled water								
$\bar{X}$	67.9	0.21	62.1	0.03	69.6	0.10	66.9	3.4
S	12.0	5.4	11.6	.7	12.9	3.6	10.4	1.6
S_r	4.43	17	3.34	2.1	4.93	1.8	4.63	5.2
Tap water								
$\bar{X}$	67.6	0.55	65.7	0.32	67.7	0.07	69.1	3.0
S	16.3	3.7	16.2	5.3	9.09	5.5	10.9	1.0
S_r	6.29	21	5.34	13	4.17	7.2	4.27	2.6

water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome because there are 12 mean recovery statistics ($\bar{X}$) (6 ampuls x 2 waters), 12 overall precision statistics (S), and 6 single-analyst precision statistics (S_r) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with $\bar{X}$, S, and S_r, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may appear to produce a significantly lower value than drinking water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in Reference 2, has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is calculated using the following statistical model. If X_{ijk} denotes the measurement reported by laboratory i, for water type j, and ampul k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where $i = 1,2,\ldots, n$
$j = 1,2$
$k = 1,2,\ldots, 6$

Model components β_j and γ_j are fixed parameters that determine the effect of water type j on the behavior of the observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampul k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor that accounts for the within-laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level (C_k) through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight-line models. Second, as will be noted below, an inherent increasing relationship exists between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation 1 is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (16)$$

Precision is related to the variability in the measurements (X_{ijk}). The variance of the data modeled by Equation 1 is

$$Var(X_{ijk}) = \left[\beta_j \cdot C_k^{\gamma_j}\right]^2 Var(L_i \cdot \varepsilon_{ijk}), \qquad (17)$$

which is an increasing function of C_k. (See Reference 2 for a complete discussion of this model.)

The accuracy and precision of Method 501.2 depend upon water type through Equations 16 and 17 and the parameters β_j and γ_j. If β_j and γ_j vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

To determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation 1 represents the basic model. However, taking natural logarithms of both sides of Equation 1, the following straight line regression model is obtained.

$$\ell n\ X_{ijk} = \ell n\ \beta_j + \gamma_j\ \ell n\ C_k + \ell n\ L_i + \ell n\ \varepsilon_{ijk} \qquad (2)$$

The parameter $\ell n\ \beta_j$ is the intercept, and γ_j is the slope of the regression line associated with water type j. It is assumed that $\ell n\ L_i$ is normally distributed with mean 0 and variance σ_L^2, that $\ell n\ \varepsilon_{ijk}$ is normally distributed with mean 0 and variance σ_ε^2, and that the $\ell n\ L_i$ and $\ell n\ \varepsilon_{ijk}$ terms are independent.

Based on Equation 2, the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameter $\ell n\ \beta_j$ (and hence β_j) and γ_j can be estimated. These estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative hypothesis, H_0 and H_A, respectively are given by:

$$H_0: \quad \ell n\ \beta_j - \ell n\ \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2 \qquad (18)$$

$$H_A: \ \ell n\ \beta_j - \ell n\ \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2 \qquad (19)$$

The null hypothesis (H_0) is tested against the alternative hypothesis (H_A) using an F-statistic. The probability of obtaining the value of an F-statistic as large as the value which was actually observed, Prob(F > F OBS), is calculated under the assumption that H_0 is true. H_0 is rejected in favor of H_A if Prob(F > F OBS) is less than 0.05.

If H_0 is not rejected, then there is no evidence in the data that the β_j vary with j or that the γ_j vary with j. Therefore, there is no evidence of an effect due to water type on the accuracy or precision of the method. If H_0 is rejected, then some linear combination of the differences ($\ell n\ \beta_j - \ell n\ \beta$) and ($\gamma_j - \gamma_1$) is statistically different from zero. This does not necessarily mean that there is an effect due to any single water type which is statistically significant. The effect due to water type is judged to be statistically significant only if one of the differences, ($\ell n\ \beta_j - \ell n\ \beta_1$) and/or ($\gamma_j - \gamma_1$), is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences ($\ell n\ \beta_j - \ell n\ \beta_1$) or ($\gamma_j - \gamma_1$) fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the differences.

The interpretation of the differences involves comparing the mean recovery and standard deviation for each water type to the mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type j, given by Equation 16, is compared to that for distilled water (j = 1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{ilk})} = \frac{\beta_j \, C_k^{\gamma_j} \, E(L_i \cdot \varepsilon_{ijk})}{\beta_1 \, C_k^{\gamma_1} \, E(L_i \cdot \varepsilon_{ilk})} = \frac{\beta_j}{\beta_1} C_k^{(\gamma_j - \gamma_1)} \qquad (20)$$

(The ratio of the standard deviations would be equivalent to Equation 20; therefore, the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in Equation 20 is a measure of the relative difference in mean recovery between water type j and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e., the constant bias), and (b) $C_k^{(\gamma_j - \gamma_1)}$, which depends on the true concentration level (i.e., the concentration dependent bias). If $(\gamma_j - \gamma_1)$ is zero, then the relative difference in mean recovery is β_j/β_1, which is independent of concentration level C_k. Then the mean recovery of water type j is β_j/β_1 x 100 percent of the mean recovery for distilled water. If $(\gamma_j - \gamma_1)$ is not zero, then the mean recovery of water type j is $([\beta_j/\beta_1] \cdot C_k^{[\gamma_j - \gamma_1]})$ x 100 percent of that for distilled water, and therefore depends on the true concentration level C_k.

To illustrate these points, consider the following example. Suppose that a significant F-value has been obtained, and the confidence intervals for all of the differences contain zero except for water type 5. For water type 5, the point estimate for $(\ell n\, \beta_5 - \ell n\, \beta_1)$ is -0.38, and the confidence interval for $(\ell n\, \beta_5 - \ell n\, \beta_1)$ is

(-0.69, -0.07). The point estimate for $(\gamma_5 - \gamma_1)$ is -0.07, and the confidence interval for $(\gamma_5 - \gamma_1)$ is (-0.04, 0.18). In this case, a statistically significant effect due to water type has been established that involves only water type 5. The practical significance of this effect is judged by considering Equation 20. The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(K_{ilk})} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \qquad (21)$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{ilk})}} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \qquad (22)$$

Because the confidence interval for $(\gamma_5 - \gamma_1)$ contains zero, this difference is assumed to be insignificant and is set to zero. Therefore, Equations 21 and 22 reduce to β_5/β_1. The point estimate for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery for distilled water. Similarly, the standard deviation for the data for water type 5 is estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend on the importance of a mean recovery (standard deviation) that is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

For a complete discussion of the statistical model and the analyses associated with the test for the effect of water types, see pages A-1 through A-17 of Reference 2. Results of the accuracy and precision comparison among the waters in the study are presented in Tables 16 through 19.

TABLE 16. EFFECT OF WATER TYPE ON CHLOROFORM ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE(GAMMA(1)) = 1.05475

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.3273	.0710

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	743.96378	743.96378		
REG(WATER/DISTILLED)	2	1.17826	.58913	2.64	.0742
ERROR	176	39.28547	.22321		
TOTAL	179	784.42751			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.3273	(-.6484 , -.0061)	.0710	(-.0136 , .1556)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 17. EFFECT OF WATER TYPE ON BROMODICHLOROMETHANE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE(GAMMA(1)) = .99429

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.2085	-.0318

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	627.87033	627.87033		
REG(WATER/DISTILLED)	2	.64422	.32211	3.89	.0221
ERROR	177	14.64013	.08271		
TOTAL	180	643.15468			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL		SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL	
2	.2085	(-.0197 ,	.3967)	-.0318	(-.0819 ,	.0184)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 18. EFFECT OF WATER TYPE ON CHLORODIBROMOMETHANE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE(GAMMA(1)) = 1.02379

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0087	-.0032

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	696.61989	696.61989		
REG(WATER/DISTILLED)	2	.00178	.00089	.01	.9851
ERROR	174	11.04830	.06350		
TOTAL	177	707.64996			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.0087	(-.1532 , .1705)	-.0032	(-.0470 , .0406)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 19. EFFECT OF WATER TYPE ON BROMOFORM ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE(GAMMA(1)) = 1.13228

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0199	-.0011

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	372.01939	372.01939		
RES(WATER/DISTILLED)	2	.00575	.00288	.14	.8736
ERROR	163	3.46686	.02127		
TOTAL	166	375.49200			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.0199	(-.1334 , .1644)	-.0011	(-.0394 , .0372)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSES ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

SECTION 6

RESULTS AND DISCUSSION

The objective of this study was to characterize the performance of Method 501.2 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision.

One measure of the performance of the method is that 19% of the 960 analytical values were rejected as outliers, which is equivalent to rejecting data from four of the twenty laboratories.

ACCURACY

The accuracy of Method 501.2 is obtained by comparing the average analyzed values to the true (calculated) values of concentration to give mean recoveries, $\bar{X}$. In the statistical summary Tables 11 through 14, individual values of accuracy as percent relative error are listed for each analyte, in both water matrices, and at each of the six concentration levels. This results in 48 separate values for the four compounds for accuracy. The weighted linear regression of mean recoveries, $\bar{X}$, versus the true concentration levels, C, provides eight values representing the percent recovery over all of the concentration levels. Table 20 presents the percent recovery for each analyte in each water matrix as measured by the slopes of the weighted linear regression equations. This is a simplified approach because the intercept portion of the regression equation is assumed to be insignificant. These values are compared to average percent recoveries calculated from the quotients $\bar{X}$:C presented in Tables 11 through 14. From Table 20,

TABLE 20. PERCENT RECOVERY STATISTICS (ACCURACY)

Compound	Slope of regression equation		Average of mean recoveries[a]	
	Distilled water	Tap water	Distilled water	Tap water
Chloroform	101	103	98	96
Bromodichloromethane	98	101	98	110
Chlorodibromomethane	102	100	101	99
Bromoform	101	103	88[b]	91[b]

[a]From Tables 16-19.

[b]Low average due to poor recovery of bromoform in low Youden pair concentrations.

it is evident that the percent recoveries (or accuracies) calculated by the two methods are in substantial agreement. The largest differences occur for bromoform where recoveries in the lowest Youden-pair concentrations were poor (64% to 77%). This also is reflected in the relatively large intercept values in the linear regression equations for mean recovery of bromoform (e.g., 3.0 and 3.4% of the average $\bar{X}$ value). In any case, the accuracy of Method 501.2 based on percent recoveries is excellent.

PRECISION

Similarly, the overall and single-analyst precisions of Method 501.2 were determined as percent relative standard deviations for each analyte, both water matrices, and at all concentration levels. The 48 individual values of % RSD, and 24 individual values of % RSD-SA are presented in the statistical summary Tables 11 through 14. The linear regression of S or S_r versus $\bar{X}$ provides values of percent relative standard deviations over the concentration range (1.7 to 170 µg/L). This reduces the separate measures of precision to eight; one value for each of four analytes in each of the two water matrices. Tables 21 and 22 present the percent relative standard deviations as measured by the slopes of the linear regression equations for the overall and single-analyst precision,

TABLE 21. OVERALL PERCENT RELATIVE STANDARD DEVIATION

Compound	Slope of regression equation		Average of percent RSD[a]	
	Distilled water	Tap water	Distilled water	Tap water
Chloroform	17[b]	26[b]	29	40
Bromodichloromethane	17	23[b]	23	35
Chlorodibromomethane	16	13[b]	24	22
Bromoform	15	16	16	17

[a]From Tables 11-14.

[b]Intercepts exceed 5% of average value.

TABLE 22. SINGLE-ANALYST PERCENT RELATIVE STANDARD DEVIATION

Compound	Slope of regression equation		Average of percent RSD-SA[a]	
	Distilled water	Tap water	Distilled water	Tap water
Chloroform	6[b]	8[b]	20	34
Bromodichloromethane	5	7[b]	6	16
Chlorodibromomethane	7	7	9	12
Bromoform	7	8	9	7

[a]From Tables 11-14.

[b]Intercepts range from 13 to 21% of average value.

respectively. Again, this is a simplified approach because the intercept portion of the regression equation is assumed to be insignificant. These values are compared to the averages of the percent relative standard deviations for each concentration as reported in Tables 11 through 14. The agreement in the precision values calculated by these two methods is much poorer than the earlier comparision of the percent recovery (or accuracy) statistics.

The greatest differences in precision calculated by the two methods occur in those cases where the magnitude of the intercept in the linear regression equations was a significant percentage (5% or more) of the average values of S or S_r. Hence, the assumption that the intercept is insignificant is not valid, and comparisons must be made by other means.

A summary of precision values at each of the Youden-pair concentrations is presented in Tables 23 and 24. A comparison of the average values of the % RSD or % RSD-SA across all of the analytes at the three levels of concentration illustrates a low precision of data in the low Youden-pair and equivalent precision values in the medium and high Youden-pairs. In every case, the precision of Method 501.2 at the drinking water level (medium Youden pair) is the best. The low average precision for chloroform and bromodichloromethane in tap water is due largely to high values for % RSD and % RSD-SA in the low concentration Youden-pair (true values of 1.76 and 2.25 µg/L). In these cases, the background concentrations of chloroform and bromodichloromethane ranged as high as 64.6 µg/L and 20 µg/L, respectively. It is suspected that the low precision is due to subtracting a variable large blank value at these low concentration levels.

EFFECT OF WATER TYPE ON ACCURACY AND PRECISION

The effect of water type on the accuracy and precision of Method 501.2 is summarized in Table 25 where the observed F values, and the probability of exceeding the F values are entered for each of the four analytes.

Only in the case of bromodichloromethane does the F-test suggest a statistically significant effect due to water type [P(F > observed F] <0.05). The null hypothesis test indicates that a statistical effect has been established due to water type for bromodichloromethane since zero is not contained within the confidence limits for ($\ell n\ \beta_j - \ell n\ \beta_1$) for either of these analytes. The practical significance was determined by applying the equations in Section 5. The equations yield a 95% confidence interval of 102% to 149% with the point estimate of 123%. Since the point estimate is within the 95% confidence interval, there is no practical significance due to water type.

TABLE 23. SUMMARY OF INTERLABORATORY PRECISION (% RSD) BY ANALYTE, WATER TYPE, AND CONCENTRATION LEVEL

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Chloroform	53.3	16.2	17.8
	Bromodichloromethane	33.6	16.2	19.5
	Chlorodibromomethane	39.8	12.6	20.3
	Bromoform	18.4	14.4	15.8
	Average of all analytes	36.3	14.9	18.4
Drinking water	Chloroform	75.8	18.2	25.5
	Bromodichloromethane	57.3	23.4	24.6
	Chlorodibromomethane	39.4	14.2	12.9
	Bromoform	18.2	16.3	15.5
	Average of all analytes	47.7	18.0	19.6

TABLE 24. SUMMARY OF SINGLE ANALYST PRECISION (% RSD-SA) BY ANALYTE, WATER TYPE, AND CONCENTRATION LEVEL

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Chloroform	45.5	8.3	5.5
	Bromodichloromethane	8.7	5.3	5.3
	Chlorodibromomethane	11.8	8.0	6.7
	Bromoform	12.2	7.6	6.5
	Average of all analytes	19.6	7.3	6.0
Drinking water	Chloroform	81.4	12.2	7.5
	Bromodichloromethane	33.7	7.9	7.8
	Chlorodibromomethane	22.4	9.3	4.9
	Bromoform	5.1	9.9	5.0
	Average of all analytes	35.7	9.8	6.3

TABLE 25. SUMMARY OF THE TESTS FOR DIFFERENCE ACROSS WATER TYPES

Compound	Observed F-value	P[F > observed F]	F-test statistically significant at the 5% level?	Statistical significance established by the 95% confidence limit?	Practical significance established by the 95% confidence limit?
Chloroform	2.64	0.07	No	-	-
Bromodichloro-methane	3.89	0.02	Yes	Yes	No
Chlorodibromo-methane	0.01	0.99	No	-	-
Bromoform	0.14	0.87	No	-	-

COMPARISION OF METHODS 501.1 AND 501.2

Methods 501.1 and 501.2 are designed to measure the same four trihalomethanes in water, the first by the purge-and-trap approach, and the second by the liquid extraction technique discussed in this report. Tables 26 and 27 compare the accuracy and precision results obtained in this study (Method 501.2) with those obtained using Method 501.1 [8]. The percent recovery (accuracy) of the two methods is comparable. When the average % RSD and average % RSD-SA values for all analytes are compared at the three Youden-pair concentrations as shown in Tables 23 and 24 for Method 501.2 and in Tables 28 and 29 for Method 501.1, it is apparent that the precision of Method 501.2 is slightly better than that of Method 501.1 except for the percent relative overall standard deviation for cholorform and dibromochloromethane in drinking water. Water type effects plays a stronger part in Method 501.2, especially for chloroform and dibromodichloromethane.

RESPONSE TO QUESTIONNAIRE

A copy of a Method 501.2 questionnaire was provided to all participating laboratories. Nine of the 20 laboratories completed the questionnaire; six others transmitted partial information. Table 30 presents a summary of the laboratory analytical conditions

TABLE 26. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR METHOD 501.2

Water type	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
Distilled Water				
Single-analyst precision	SR = 0.06X + 0.76	SR = 0.05X + 0.07	SR = 0.07X + 0.09	SR = 0.07X + 0.24
Overall precision	S = 0.17X + 0.65	S = 0.17X + 0.31	S = 0.16X + 0.47	S = 0.15X + 0.17
Accuracy	X = 1.01C + 0.14	S = 0.98C + 0.02	S = 1.02C + 0.07	X = 1.01C - 2.29
Tap Water				
Single-analyst precision	SR = 0.08X + 1.33	SR = 0.07X + 0.67	SR = 0.07X + 0.30	SR = 0.08X - 0.11
Overall precision	S = 0.26X + 0.60	S = 0.23X + 0.86	S = 0.13X + 0.50	S = 0.16X + 0.11
Accuracy	X = 1.03X - 0.37	X = 1.01C + 0.51	X = 1.00C - 0.05	X = 1.03C - 2.08

X = mean recovery.
C = true value for the concentration.

TABLE 27. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR METHOD 501.1

Water type	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
Distilled Water				
Single-analyst precision	SR = 0.10X + 0.13	SR = 0.15X + 0.05	SR = 0.16X + 0.06	SR = 0.19X - 0.25
Overall precision	S = 0.20X + 0.20	S = 0.23X + 0.15	S = 0.26X + 0.35	S = 0.28X + 0.63
Accuracy	X = 0.92C + 0.04	S = 0.95C - 0.04	S = 0.99C - 0.08	X = 1.03C - 1.48
Tap Water				
Single-analyst precision	SR = 0.11X + 0.03	SR = 0.15X + 0.18	SR = 0.18X + 0.13	SR = 0.23X - 0.05
Overall precision	S = 0.18X + 0.74	S = 0.22X + 0.38	S = 0.27X + 0.07	S = 0.32X + 0.47
Accuracy	X = 1.02C - 0.37	X = 1.02C + 0.08	X = 1.04C - 0.16	X = 1.08C - 1.75

X = mean recovery.
C = true value for the concentration.

TABLE 28. SUMMARY OF PRECISION (PERCENT RSD) BY ANALYTE, WATER TYPE, AND CONCENTRATION RANGE (METHOD 501.1)

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Chloroform	41.7	9.7	29.9
	Bromodichloromethane	39.1	13.2	33.7
	Chlorodibromomethane	68.3	16.8	32.4
	Bromoform	43.3	24.5	32.5
	Average of all analytes	48.1	16.1	32.1
Drinking water	Chloroform	70.9	16.9	16.2
	Bromodichloromethane	56.3	15.1	30.8
	Chlorodibromomethane	35.2	23.1	30.3
	Bromoform	44.1	27.8	36.7
	Average of all analytes	51.6	20.7	28.5

TABLE 29. SUMMARY OF PRECISION (PERCENT RSD-SA)[a] BY ANALYTE, WATER TYPE, AND CONCENTRATION RANGE (METHOD 501.1)

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Chloroform	22.8	8.9	10.8
	Bromodichloromethane	9.9	10.4	20.1
	Chlorodibromomethane	22.5	13.0	19.0
	Bromoform	13.3	16.6	21.1
	Average of all analytes	17.1	12.2	17.8
Drinking water	Chloroform	62.6	15.7	8.1
	Bromodichloromethane	30.8	9.5	21.5
	Chlorodibromomethane	33.7	15.6	21.2
	Bromoform	21.8	22.9	23.1
	Average of all analytes	37.2	15.9	18.5

[a]Average of Youden pairs.

TABLE 30. LABORATORY ANALYTICAL CONDITIONS

Laboratory code	Liquid extractant	Gas chromatograph	Temperature program, °C	Carrier gas/ flow, mL/min	Column packing	Column
1	Pentane	H-P 5880A	45°-12 min 1°/min to 100°	95% A-5% CH_4 /25	6% OV-11 4% SP-2100	-
2	Isooctane	Tracor 550	50°-isothermal	95% A-5% CH_4 /60	3% SP-1000	2 m x 2 mm
4	Hexane	H-P 5713	65°-isothermal	95% A-5% CH_4 /30	3% SP-1000	6' x 2 mm-glass
5	Hexane	P-E 3920	70°-isothermal	95% A-5% CH_4	3% SP-1000	6' x 2 mm-glass
6	Methylcyclohexane	H-P 5880A	100°-isothermal	95% A-5% CH_4 /60	3% SP-1000	-
7	Hexane	H-P 5710	80°-isothermal	95% A-5% CH_4 /80	3% SP-1000	6' x 4 mm-glass
8	Hexane	Varian 3700	50°-isothermal	95% A-5% CH_4 /60	3% SP-1000	6' x 2 mm-glass
9	Isooctane	-	-	-	-	-
11	Pentane	Varian 2700	50°-2 min 20°/min to 200°	N_2/30	3% SP-1000	-
12	Pentane	H-P	-	-	-	-
14	Hexane	-	65°-isothermal	N_2/24	3% SP-1000	6' x 2 mm
15	Hexane	-	-	-	-	-
18	Hexane	Tracor 560	65°-isothermal	N_2/24	3% SP-1000	6' x 2 mm-glass
19	Cyclohexane	HP-5730A	60°-isothermal	95% A-5% CH_4 /60	3% SP-1000	-

employed by the reporting laboratories. All but one of the reporting laboratories employed 6 ft x 2 mm ID glass columns. Laboratory 7 used a 6 ft x 4mm ID column. All but one of the reporting laboratories used a 3% SP1000 on 100/120 mesh Supelcoport packing. Laboratory 1 employed 6% OV-11/4% SP2100 on Supelcoport (100/120 mesh). Two of the reporting laboratories (1, 11) used temperature programming; the remainder employed isothermal column temperatures ranging from 50°C to 100°C. Eight of the reporting laboratories employed 5% methane in argon as the carrier gas; three others used nitrogen gas (11, 14, 18). Flow rates of carrier gas varied from 24 mL/min to 80 mL/min.

Seven of the reporting laboratories, used hexane as the extraction solvent, three used pentane, two used isooctane, and one laboratory each employed cyclohexane and methylcyclohexane. The laboratories that used isooctane (2, 9) were at high altitude and experienced boiling of n-pentane during the liquid/liquid extraction step. Some laboratories using n-hexane encountered contamination from chloroform and bromoform but were able to correct for these backgrounds. One laboratory suspected that partitioning in the extraction process could lead to loss of chloroform. The laboratory using cyclohexane (19) stated that this solvent was readily contaminated by chloroform and bromoform in the laboratory ambient air.

No laboratory reported problems in preparation of standards, but one laboratory stated that there was a wider variability in the standardization results than when Method 501.1 was employed. Only one laboratory reported problems with poor detector sensitivity. This was partially resolved by resorting to temperature programming of the chromatographic column (2 min hold at 50°C followed by 20°C/min to 200°C). Four of the laboratories reported no problems in the linearity of the electron capture detector response to the trihalomethanes over the concentration range (2 to 175 µg/L). Two laboratories (8, 11) encountered nonlinearity above 200 µg/L.

Laboratory 11 diluted the higher concentration Youden-pair solutions to get back to the linear range. Laboratory 5 reported that only chloroform analyses were linear, while response to the other three trihalomethanes fell off at high concentrations. Laboratory 4 stated that all four analytes gave different shaped calibration curves. A wide variety of calibration methods were reported, but none of the laboratories reported problems of day-to-day variation in detector sensitivity.

Other problems encountered included a negative response (drop in baseline) immediately before the chloroform peak (Laboratory 5). This problem was solved by the laboratory by redrawing the baseline before quantitation. Laboratory 7 had to increase carrier gas flow rate to 80 mL/min to get reported retention times. Laboratory 19 stated that laboratory ambient air concentrations of chloroform and methylene chloride limited the detection limit for chloroform.

Recommendations received from the participating laboratories included:

- Use 2-mm I.D. glass columns instead of 4-mm, and operate isothermally at 70°C and at a carrier gas flow rate of 30 mL/min. (Laboratory 5)

- Use Method 601 column (1% SP1000 on Carbopak B) and temperature program from 70°C to 220°C. (Laboratory 11)

- Include better "sample handling" techniques in the method writeup. (Laboratory 19)

- Use Method 501.2 in perference to Method to 501.1 because it is much faster, and increase column temperature to 100°C to further speed-up the method. (Laboratory 6)

It is easily seen that Method 501.2 is rugged. The analysts used various equipment and conditions yet still generated acceptable results.

REFERENCES

1. Youden, W. J. Statistical Techniques for Collaborative Tests. Association of Official Analytical Chemists, Inc., Washington, D.C., 1969. 64 pp.

2. Outler, E. C. and J. H. McCreary, Interlaboratory Method Validation Study: Program Documentation, Battelle Columbus Laboratories, 1982.

3. Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water. ASTM D2777-77, Annual Book of ASTM Standards, Part 31. American Society for Testing and Materials, Philadelphia, Pennsylvania, 1980. pp. 16-28.

4. Standard Practice for Dealing with Outlying Observations. ANSI/ASTM E178-80, Annual Book of ASTM Standards, Part 41. American Society for Testing and Materials, Philadelphia, Pennsylvania, 1980. pp. 206-231.

5. Youden, W. J. Statistical Manual of the AOAC. The Association of Official Analytical Chemists, Washington, D.C., 1975.

6. Thompson, W. R. On a Criterion for the Rejection of Observations and the Distribution of the Ratio of the Deviation to the Sample Standard Deviations. The Annals of Mathematical Statistics, AASTA 6:214-219, 1935.

7. Britton, P. W. Statistical Basis for Laboratory Performance Evaluation Limits. Presented at the 142nd Joint Statistical Meeting, Cincinnati, Ohio, August 17, 1982.

8. Warner, B. J., et al. Determination of Trihalomethanes by the Purge and Trap Method (Method 501.1): Validation of Analytical Method. U.S. Environmental Protection Agency, Cincinnati, Ohio, contract 68-03-2856 in publication.

APPENDIX A

THE ANALYSIS OF TRIHALOMETHANES IN DRINKING WATER BY LIQUID/LIQUID EXTRACTION METHOD 501.2

U. S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
CINCINNATI, OHIO 45268

November 6, 1979

FOREWORD

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati, at the request of the Office of Drinking Water, with cooperation from the Technical Support Division, ODW and the Municipal Environmental Research Laboratory. Their comments and suggestions on updating the September 9, 1977, Interim Method as well as those of the Health Effects Research Laboratory are gratefully acknowledged.

The procedure represents the current state-of-the-art, but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction

1. Scope

1.1 This method (1,2) is applicable only to the determination of four trihalomethanes, i.e., chloroform, bromodichloromethane, chlorodibromomethane, and bromoform in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water.

1.2 For compounds other than the above-mentioned trihalomethanes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples as described in (3) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (4).

1.3 Qualitative analyses using GC/MS or the purge and trap method (5) must be performed to characterize each raw source water if peaks appear as interferences in the raw source analysis.

1.4 The method has been shown to be useful for the trihalomethanes over a concentration range from approximately 0.5 to 200 µg/l. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. Summary

2.1 Ten milliliters of sample are extracted one time with 2 ml of solvent. Three µl of the extract are then injected into a gas

chromatograph equipped with a linearized electron capture detector for separation and analysis.

2.2 The extraction and analysis time is 10 to 50 minutes per sample depending upon the analytical conditions chosen. (See Table 1 and Figures 1, 2, and 3.)

2.3 Confirmatory evidence is obtained using dissimilar columns and temperature programming. When component concentrations are sufficiently high (>50 µg/l), halogen specific detectors may be employed for improved specificity.

2.4 Unequivocal confirmatory analyses at high levels (>50 µg/l) can be performed using GC/MS in place of the electron capture detector. At levels below 50 µg/l, unequivocal confirmation can only be performed by the purge and trap technique using GC/MS (4, 5).

2.5 Standards dosed into organic free water and the samples are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.

2.6 The concentration of each trihalomethane is summed and reported as total trihalomethanes in µg/l.

3. Interferences

3.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed before a new bottle of solvent is used to extract samples. Indirect daily checks on the extracting solvent are obtained by monitoring the sample blanks (6.4.10). Whenever an interference is noted in the sample blank, the analyst should reanalyze the extracting solvent. The extraction solvent should be discarded

whenever a high level (>10 µg/l) of interfering compounds are traced to it. Low level interferences generally can be removed by distillation or column chromatography (6); however, it is generally more economical to obtain a new source of solvent or select one of the approved alternative solvents listed in Section 5.1. Interference free solvent is defined as a solvent containing less than 0.4 µg/l individual trihalomethane interference. Protect interference-free solvents by storing in a non-laboratory area known to be free of organochlorine solvents. Subtracting blank values is not recommended.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal on the sample bottle during shipment and storage. The sample blank (6.4.10) is used to monitor for this problem.

3.3 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds and, in addition, extracts the polar organic components of the sample with varying efficiencies. In order to perform the trihalomethane analysis as rapidly as possible with sensitivities in the low µg/l range, it is necessary to use the semi-specific electron capture detector and chromatographic columns which have relatively poor resolving power. Because of these concessions, the probability of experiencing chromatographic interferences is high. Trihalomethanes are primarily products of the chlorination process and generally do not appear in the raw source water. The absence of peaks in the raw

source water analysis with retention times similar to the trihalomethanes is generally adequate evidence of an interference-free finished drinking water analysis. Because of these possible interferences, in addition to each finished drinking water analysis, a representative raw source water (6.4.5) must be analyzed. When potential interferences are noted in the raw source water analysis, the alternate chromatographic columns must be used to reanalyze the sample set. If interferences are still noted, qualitative identifications should be performed according to Sections 2.3 and 2.4. If the peaks are confirmed to be other than trihalomethanes and add significantly to the total trihalomethane value in the finished drinking water analysis, then the sample set must be analyzed by the purge and trap method (5).

4. Apparatus

4.1 Extraction vessel - A 15 ml total volume glass vessel with a Teflon lined screw-cap is required to efficiently extract the samples.

4.1.1 For samples that do not form emulsions 10 ml screw-cap flasks with a Teflon faced septum (total volume is ml) are recommended.

Flasks and caps - Pierce - #13310 or equivalent

Septa - Teflon silicone - Pierce #12718 or equivalent.

4.1.2 For samples that form emulsions (turbid source water) 15 ml screw cap centrifuge tubes with a Teflon cap liner are recommended.

Centrifuge tube - Corning 8062-15 or equivalent.

4.2 Sampling containers - 40 ml screw cap sealed with Teflon faced silicone septa.

Vials and caps - Pierce #13075 or equivalent.

Septa - Pierce #12722 or equivalent.

4.3 Micro syringes - 10, 100 µl.

4.4 Micro syringe - 25 µl with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.

4.5 Syringes - 10 ml glass hypodermic with luerlok tip (2 each).

4.6 Syringe valve - 2-way with luer ends (2 each) - Hamilton #86570-1PM1 or equivalent.

4.7 Pipette - 2.0 ml transfer.

4.8 Glass stoppered volumetric flasks - 10 and 100 ml.

4.9 Gas chromatograph with linearized electron capture detector. (Recommended option - temperature programmable. See Section 4.12).

4.10 Column A - 4 mm ID x 2m long glass packed with 3% SP-1000 on Supelcoport (100/120 mesh) operated at 50°C with 60 ml/min flow. (See Figure 1 for a sample chromatogram and Table 1 for retention data).

4.11 Column B - 2 mm ID x 2m long glass packed with 10% squalane on Chromosorb WAW (80/100 mesh) operated at 67°C with 25 ml/min flow. This column is recommended as the primary analytical column. Trichloroethylene, a common raw source water contaminate, coelutes with bromodichloromethane. (See Figure 2 for a sample chromatogram and Table 1 for retention data.)

4.12 Column C - 2 mm ID x 3m long glass packed with 6% OV-11/4% SP-2100 on Supelcoport (100/120 mesh) temperature program 45°C for 12 minutes, then program at 1°/minute to 70°C with a 25 ml/min

flow. (See Figure 3 for a sample chromatogram and Table I for retention data.)

4.13 Standard storage containers - 15 ml amber screw-cap septum bottles with Teflon faced silicone septa.

Bottles and caps - Pierce #19830 or equivalent.

Septa - Pierce #12716 or equivalent.

5. Reagents

5.1 Extraction solvent - (See 3.1).

Recommended - Pentane[a]

Alternative - hexane, methylcyclohexane or 2,2,4-trimethylpentane.

[a]Pentane has been selected as the best solvent for this analysis because it elutes, on all of the columns, well before any of the trihalomethanes. High altitudes or laboratory temperatures in excess of 75°F may make the use of this solvent impractical. For these reasons, alternative solvents are acceptable; however, the analyst may experience baseline variances in the elution areas of the trihalomethanes due to coelution of these solvents. The degree of difficulty appears to be dependent upon the design and condition of the electron capture detector. Such problems should be insignificant when concentrations of the coeluting trihalomethane are in excess of 5 µg/l.

5.2 Methyl alcohol - ACS Reagent Grade

5.3 Free and combined chlorine reducing agents - Sodium thiosulfate ACS Reagent Grade - sodium sulfite ACS Reagent Grade.

5.4 Activated carbon - Filtrasorb - 200, available from Calgon Corporation, Pittsburgh, PA, or equivalent.

5.5 Standards:[b]

5.5.1 Bromoform 96% - available from Aldrich Chemical Company.

5.5.2 Bromodichloromethane 97% - available from Aldrich Chemical Company.

5.5.3 Chlorodibromomethane - available from Columbia Chemical, Incorporated, Columbia, S.C.

5.5.4 Chloroform 99% - available from Aldrich Chemical Company.

5.6 Organic-free water - Organic-free water is defined as water free of interference when employed in the procedure described herein.

5.6.1 Organic-free water is generated by passing tap water through a carbon filter bed containing carbon. Change the activated carbon whenever the concentration of any trihalomethane exceeds 0.4 µg/l.

5.6.2 A Millipore Super-Q Water System or its equivalent may be used to generate organic-free deionized water.

5.6.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant free inert gas through the water at 100 ml/minute for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

5.6.4 Test organic free water each day it is used by analyzing it according to Section 7.

[b]As a precautionary measure, all standards must be checked for purity by boiling point determinations or GC/MS assays.

5.7 Standard stock solutions

5.7.1 Fill a 10.0 ml ground glass stoppered volumetric flask with approximately 9.8 ml of methyl alcohol.

5.7.2 Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces dry.

5.7.3 Weigh the unstoppered flask to the nearest 0.1 mg.

5.7.4 Using a 100 µl syringe, immediately add 2 to 3 drops of the reference standard to the flask, then reweigh. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask.

5.7.5 Dilute to volume, stopper, then mix by inverting the flask several times.

5.7.6 Transfer the standard solution to a dated and labeled 15 ml screw-cap bottle with a Teflon cap liner.

NOTE: Because of the toxicity of trihalomethanes, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

5.7.7 Calculate the concentration in micrograms per microliter from the net gain in weight.

5.7.8 Store the solution at $4^{o}C$.

NOTE: All standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

5.8 Aqueous calibration standard precautions

5.8.1 In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

a. Do not inject more than 20 µl of alcoholic standards into 100 ml of organic-free water.

b. Use a 25 µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

c. Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.

d. Mix aqueous standards by inverting the flask three times only.

e. Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask as directed in Section 7.

f. Never use pipets to dilute or transfer samples and aqueous standards.

g. Aqueous standards, when stored with a headspace, are not stable and should be discarded after one hour. Aqueous standards can be stored according to Sections 6.4.9 and 7.2.

5.9 Calibration standards

5.9.1 Prepare, from the standard stock solutions, a multicomponent secondary dilution mixture in methyl alcohol so that a 20 µl injection into 100 ml of organic-free water will generate a calibration standard which produces a response close (± 25%) to that of the unknown. (See 8.1).

5.9.2 Alternative calibration procedure

5.9.2.1 Construct a calibration curve for each trihalomethane containing a minimum of 3 different concentrations. Two of the concentrations must bracket each unknown.

5.9.3 Extract and analyze the aqueous calibration standards in the same manner as the unknowns.

5.9.4 Other calibration procedures (7) which require the delivery of less than 20 µl of methanolic standards to 10.0 ml volumes of water contained in the sample syringe are acceptable only if the methanolic standard is delivered by the solvent flush technique (8).

5.10 Quality Check Standard Mixture

5.10.1 Prepare, from the standard stock solutions, a secondary dilution mixture in methyl alcohol that contains 10.0 ng/µl of each compound. (See 5.7.6 and 5.7.8).

5.10.2 Daily, prepare and analyze a 2.0 µg/l aqueous dilution from this mixture by dosing 20.0 µl into 100 ml of organic-free water (See Section 8.1).

6. Sample Collection and Handling

6.1 The sample containers should have a total volume of at least 25 ml.

6.1.1 Narrow-mouth screw-cap bottles with the TFE fluorocarbon faced silicone septa cap liners are strongly recommended.

6.2 Glassware Preparation

6.2.1 Wash all sample bottles, TFE seals, and extraction flasks in detergent. Rinse with tap water and finally with distilled water.

6.2.2 Allow the bottles and seals to air dry, then place in an 105°C oven for 1 hour, then allow to cool in an area known to be free of organics.

NOTE: Do not heat the TFE seals for extended periods of time (>1 hour) because the silicone layer slowly degrades at 105°C.

6.2.3 When cool, seal the bottles using the TFE seals that will be used for sealing the samples.

6.3 Sample stabilization - A chemical reducing agent (Section 5.3) is added to all samples in order to arrest the formation of additional trihalomethanes after sample collection (7,9) and to eliminate the possibility of free chlorine reacting with impurities in the extraction solvent to form interfering organohalides. DO NOT ADD THE REDUCING AGENT TO SAMPLES AT COLLECTION TIME WHEN DATA FOR MAXIMUM TRIHALOMETHANE FORMATION IS DESIRED. If chemical stabilization is employed, then the reagent is also added to the blanks. The chemical agent (2.5 to 3 mg/40 ml) is added in

crystalline form to the empty sample bottle just prior to shipping to the sampling site. If chemical stabilizaton is not employed at sampling time then the reducing agent is added just before extraction.

6.4 Sample Collection

6.4.1 Collect all samples in duplicate.

6.4.2 Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is filled.

6.4.3 Seal the bottle so that no air bubbles are entrapped in it.

6.4.4 Maintain the hermetic seal on the sample bottle until analysis.

6.4.5 The raw source water sample history should resemble the finished drinking water. The average retention time of the finished drinking water within the water plant should be taken into account when sampling the raw source water.

6.4.6 Sampling from a water tap.

6.4.6.1 Turn on the water and allow the system to flush until the temperature of the water has stabilized. Adjust the flow to about 500 ml/minute and collect duplicate samples from the flowing stream.

6.4.7 Sampling from an open body of water.

6.4.7.1 Fill a 1-quart wide-mouth bottle with sample from a representative area. Carefully fill duplicate sample bottles from the 1-quart bottle as in 6.4.

6.4.8 If a chemical reducing agent has been added to the sample bottles, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

6.4.9 Sealing practice for septum seal screw cap bottles.

6.4.9.1 Open the bottle and fill to overflowing. Place on a level surface. Position the TFE side of the septum seal upon the convex sample meniscus and seal the bottle by screwing the cap on tightly.

6.4.9.2 Invert the sample and lightly tap the cap on a solid surface. The absence of entrapped air indicates a successful seal. If bubbles are present, open the bottle, add a few additional drops of sample, then reseal bottle as above.

6.4.10 Sample blanks

6.4.10.1 Prepare blanks in duplicate at the laboratory by filling and sealing sample bottles with organic-free water just prior to shipping the sample bottles to the sampling site.

6.4.10.2 If the sample is to be stabilized, add an identical amount of reducing agent to the blanks.

6.4.10.3 Ship the blanks to and from the sampling site along with the sample bottles.

6.4.10.4 Store the blanks and the samples, collected at a given site (sample set), together in a protected area known to be free from contamination. A sample set is defined as all the samples collected at a given site (i.e., at a water treatment plant, duplicate raw source water, duplicate finished water and the duplicate sample blanks comprise the sample set).

6.5 When samples are collected and stored under these conditions, no measurable loss of trihalomethanes has been detected over extended periods of time (7). It is recommended that the samples be analyzed within 14 days of collection.

7. Extraction and Analysis

7.1 Remove the plungers from two 10-ml syringes and attach a closed syringe valve to each.

7.2 Open the sample bottle[c] (or standard) and carefully pour the sample into one of the syringe barrels until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residue air while adjusting the sample volume to 10.0 ml. Close the valve.

7.3 Fill the second syringe in an identical manner from the same sample bottle. This syringe is reserved for a replicate analysis (see 8.3 and 8.4).

[c] If for any reason the chemical reducing agent has not been added to the sample, then it must be added just prior to analyses at the rate of 2.5 to 3 mg/40 ml or by adding 1 mg directly to the sample in the extracion flask.

7.4 Pipette 2.0 ml of extraction solvent into a clean extraction flask.

7.5 Carefully inject the contents of the syringe into the extraction flask.

7.6 Seal with a Teflon faced septum.

7.7 Shake vigorously for 1 minute.

7.8 Let stand until the phases separate (~ 60 seconds).

7.8.1 If the phases do not separate on standing then centrifugation can be used to facilitate separation.

7.9 Analyze the sample by injecting 3.0 µl (solvent flush technique, (8)) of the upper (organic) phase into the gas chromatograph.

8. Analytical Quality Control

8.1 A 2 µg/l quality check standard (See 5.10) should be extracted and analyzed each day before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at 5 times the noise level are obtained from these data. In addition, the data obtained from the quality check standard can be used to estimate the concentration of the unknowns. From this information the appropriate standards can be determined.

8.2 Analyze the sample blank and the raw source water to monitor for potential interferences as described in Sections 3.1, 3.2, and 3.3.

8.3 Spiked samples

8.3.1 For those laboratories analyzing more than 10 samples a day, each 10th sample analyzed should be a laboratory-generated

spike which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample in organic-free water as described in 5.9.

8.3.2 In those laboratories analyzing less than 10 samples daily, each time the analysis is performed, analyze at least one laboratory generated spike sample which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample in organic-free water as described in Section 5.9.

8.3.3 Maintain an up-to-date log on the accuracy and precision data collected in Sections 8.3 and 8.4. If results are significantly different than those cited in Section 10.1, the analyst should check out the entire analysis scheme to determine why the laboratory's precision and accuracy limits are greater.

8.4 Randomly select and analyze 10% of all samples in duplicate.

8.5 Analyze all samples in duplicate which appear to deviate more than 30% from any established norm.

8.6 Quarterly, spike an EMSL-Cincinnati trihalomethane quality control sample into organic-free water and analyze.

8.6.1 The results of the EMSL trihalomethane quality control sample should agree within 20% of the true value for each trihalomethane. If they do not, the analyst must check each step in the standard generation procedure to solve the problem.

8.7 It is important that the analyst be aware of the linear response characteristics of the electron capture system that is utilized. Calibration curves should be generated and rechecked quarterly for each trihalomethane over the concentration range encountered in the samples in order to confirm the linear response range of the system. Quantitative data cannot be calculated from non-linear responses. Whenever non-linear responses are noted, the analyst must dilute the sample for reanalysis.

8.8 Maintain a record of the retention times for each trihalomethane using data gathered from spiked samples and standards.

8.8.1 Daily calculate the average retention time for each trihalomethane and the variance encountered for the analyses.

8.8.2 If individual trihalomethane retention time varies by more than 10% over an eight hour period or does not fall within 10% of an established norm, the system is "out of control." The source of retention data variation must be corrected before acceptable data can be generated.

9. Calculations

9.1 Locate each trihalomethane in the sample chromatogram by comparing the retention time of the suspect peak to the data gathered in 8.8.1. The retention time of the suspect peak must fall within the limits established in 8.8.1 for a single column identification.

9.2 Calculate the concentration of each trihalomethane by comparing the peak heights or peak areas of the samples to those of the standards. Round off the data to the nearest µg/l or two significant Figures.

TABLE 1

Retention Times for Trihalomethanes

Trihalomethane	Retention Time Minutes Column A	Column B	Column C
Chloroform	1.0	1.3	4.9
bromodichloromethane	1.5	2.5[d]	11.0
chlorodibromomethane (dibromochloromethane)	2.6	5.6	23.1
bromoform	5.5	10.9	39.4

[d]On this column, trichloroethylene, a common raw source water contaminate, coelutes with bromodichloromethane.

Table II
Single Laboratory Accuracy and Precision

Compound	Dose level ug/l	Number of samples	Mean ug/l	Precision Relative Standard Deviation,%	Accuracy % Recovery
$CHCl_3$	9.1	5	10	11	110
$CHCl_3$	69	3	73	5.3	106
$CHBrCl_2$	1.2	5	1.3	9.8	108
$CHBrCl_2$	12	2	15	1.4	125
$CHBr_2Cl$	2.7	5	2.0	17	74
$CHBr_2Cl$	17	3	16	9.9	94
$CHBr_3$	2.9	5	2.2	10	76
$CHBr_3$	14	3	16	12	114

REFERENCES

1. Mieure, J. P., "A Rapid and Sensitive Method for Determining Volatile Organohalides in Water," Journal AWWA, 69, 60, 1977.

2. Reding, R., etal. "THM's in Drinking Water: Analysis by LLE and Comparison to Purge and Trap", Organics Analysis in Water and Wastewater, STP 686 ASTM, 1979.

3. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," Analytical Quality Control Laboratory, National Environmental Research Center, Cincinnati, Ohio, June 1972.

4. Budde, W.L., J.W. Eichelberger, "Organic Analysis Using Gas Chromatography-Mass Spectrometry," Ann Arbor Science, Ann Arbor, Michigan, 1979.

5. "The Analysis of Trihalomethanes in Finished Water by the Purge and Trap Method," Environmental Monitoring and Support Laboratory, Environmental Research Center, Cincinnati, Ohio, 45268, May 15, 1979.

6. Richard, J.J.; G.A. Junk, "Liquid Extraction for Rapid Determination of Halomethanes in Water," Journal AWWA, 69, 62, January 1977.

7. Brass, H.J., et al., "National Organic Monitoring Survey: Sampling and Purgeable Organic Compounds, Drinking Water Quality Through Source Protection," R. B. Pojasek, Editor, Ann Arbor Science, p. 398, 1977.

8. White, L.D., et al. "Convenient Optimized Method for the Analysis of Selected Solvent Vapors in Industrial Atmosphere," AIHA Journal, Vol. 31, p. 225, 1970.

9. Kopfler, F.C., et al. "GC/MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) or Drinking Water, Identification and Analysis of Organic Pollutants in Water," L. H. Keith, Editor, Ann Arbor Science, p. 87, 1976.

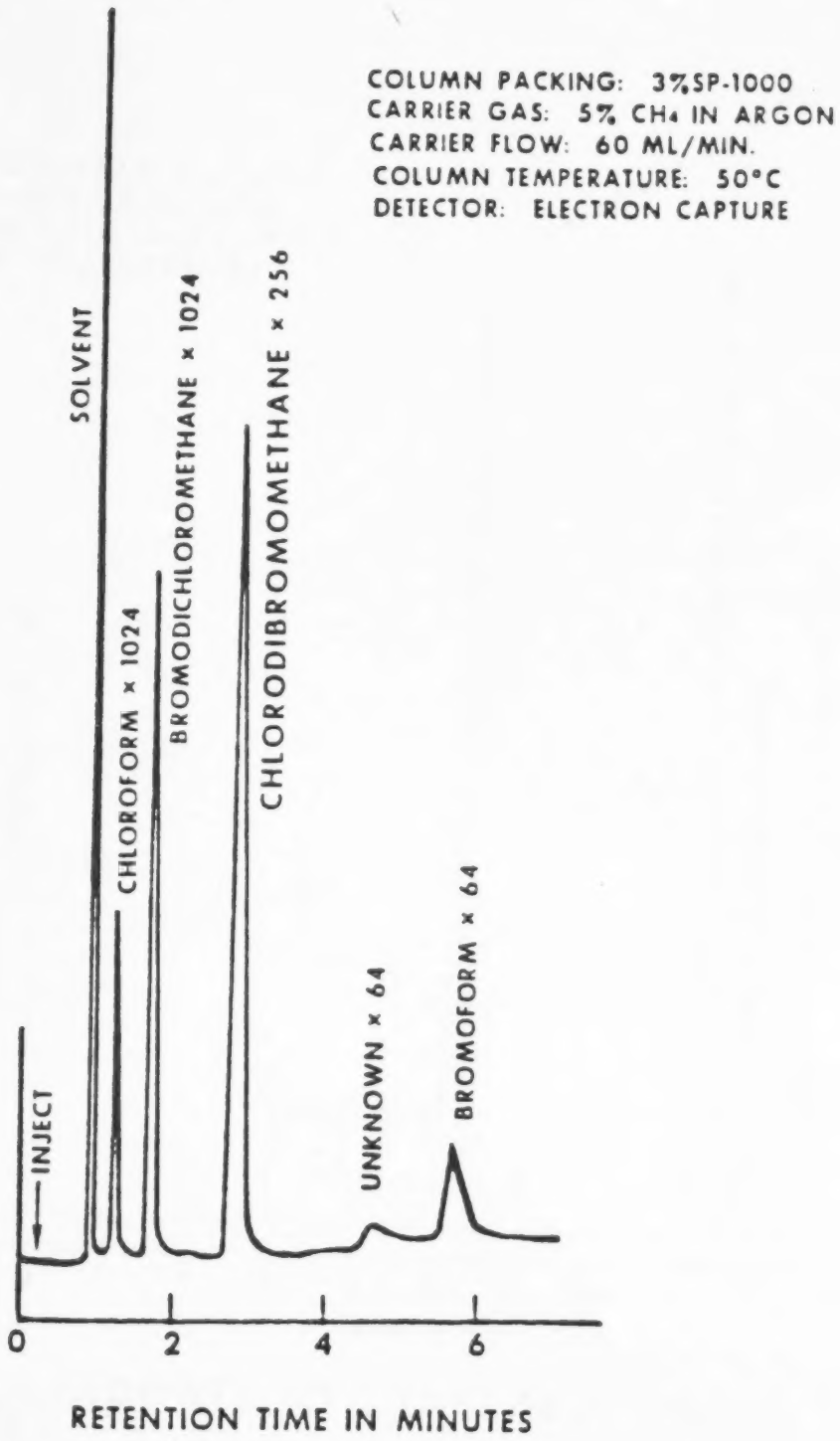


FIGURE 1. FINISHED WATER EXTRACT

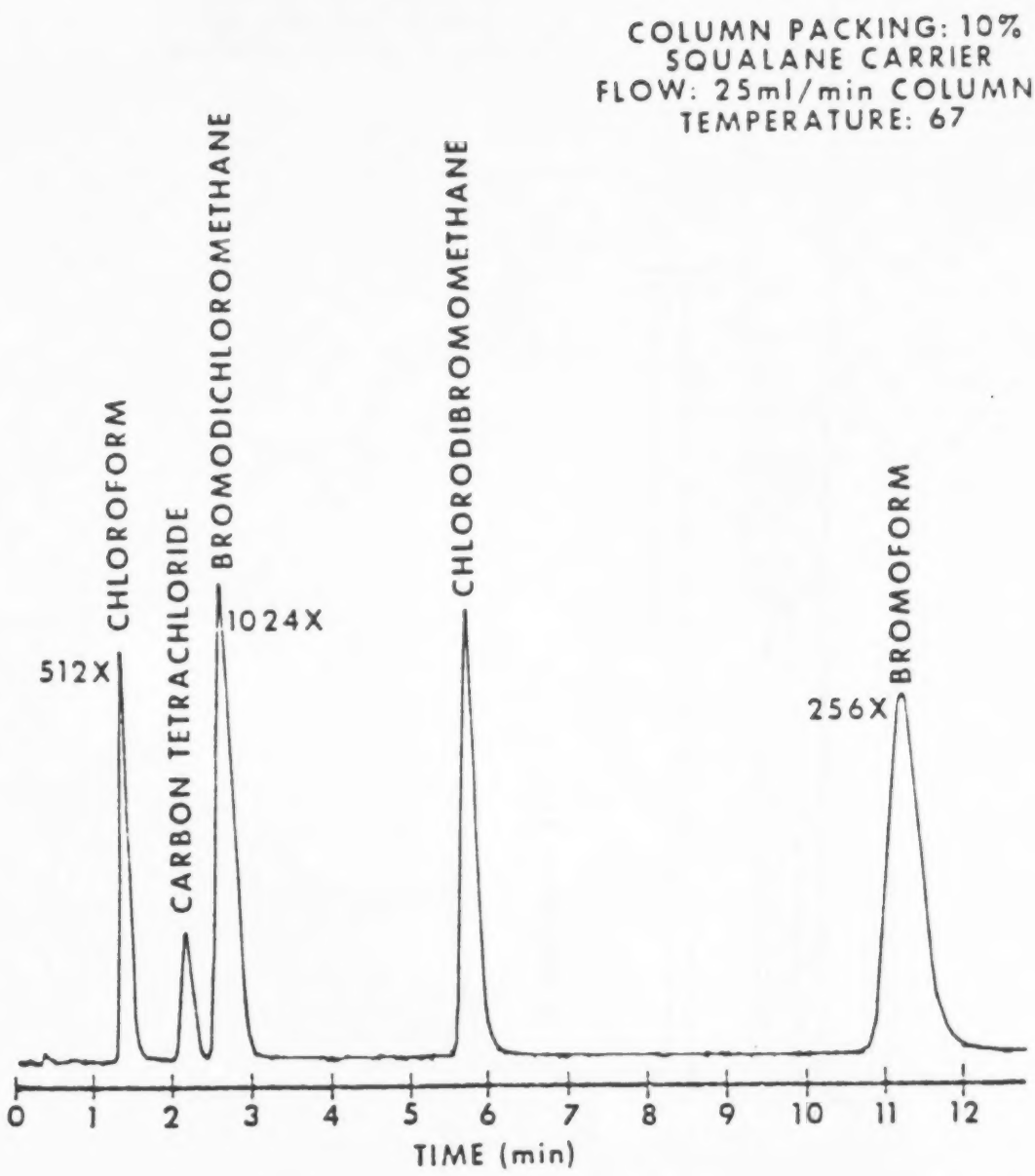


FIGURE 2. EXTRACT OF STANDARD

APPENDIX B

TESTS OF THE LINEARITY OF METHOD 501.2 FOR ANALYSIS OF TRIHALOMETHANES

In January 1981, prior to the study conference, MRC analysts conducted a brief study on EPA Method 501.2 to establish calibration curves and demonstrate linearity of the analytical method. Standards for chloroform, bromodichloromethane, chlorodibromomethane, and bromoform were prepared in methanol. The alcoholic standard solutions were spiked into drinking water and mixed three times by inversion. Ten-mL aliquots were withdrawn and extracted with 2 mL of hexane according to the Method 501.2 procedure. The extract was analyzed by gas chromatography for the trihalomethanes.

Pentane and hexane were investigated as extraction solvents, and both were found to be contaminated with trihalomethanes. Hexane was chosen as the extraction solvent because it was less contaminated than pentane. The contamination of trihalomethanes in hexane could not be removed by purging with helium or by passing the solvent through columns of Florisil®, alumina, or Tenax-GC®. Hexane blank values for the trihalomethanes were therefore subtracted from the values obtained on analysis of the standards.

The following gas chromatographic conditions were employed in the verification study:

Instrument - Perkin-Elmer 3920B chromatograph with an electron capture detector

Column - 6 ft x 1/4 in., 4-mm ID glass packed with 3% SP-1000 on 60/80 mesh Chromosorb WAW

Temperature - Column: 70°C, isothermal
Injection port: 250°C
Detector: 300°C

Carrier gas - 95% Argon/5% Methane at 30 mL/min flow

Observed retention times were: chloroform - 1.72 min
bromodichloromethane - 3.30 min
chlorodibromomethane - 7.17 min
bromoform - 16.57 min

The concentrations of the trihalomethanes in the standards are presented in Table B-1 while the plots of the resultant analytical data are presented in Figures B-1 through B-4 for each of the analytes.

TABLE B-1. CONCENTRATIONS OF TRIHALOMETANES IN STANDARDS (µg/L)

Standards	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
A-C	180.0	165.0	219.0	259.5
E-G	120.0	110.0	146.0	173.0
H-J	54.55	50.0	66.35	78.65
K-M	27.3	25.0	33.2	39.3
N-P	10.9	10.0	13.3	15.7
Q-S	5.5	5.0	6.6	7.9

As a result of this brief study, the linearity of EPA Method 501.2 for analysis of trihalomethanes was verified. However, close examination of Figures B-1 through B-4 indicates that, for all analytes, the highest concentration values fell below the straight line. This could mean that detector saturation is approached at concentrations in excess of 160 to 180 µg/L. The highest concentration employed in the validation study was 174 µg/L.

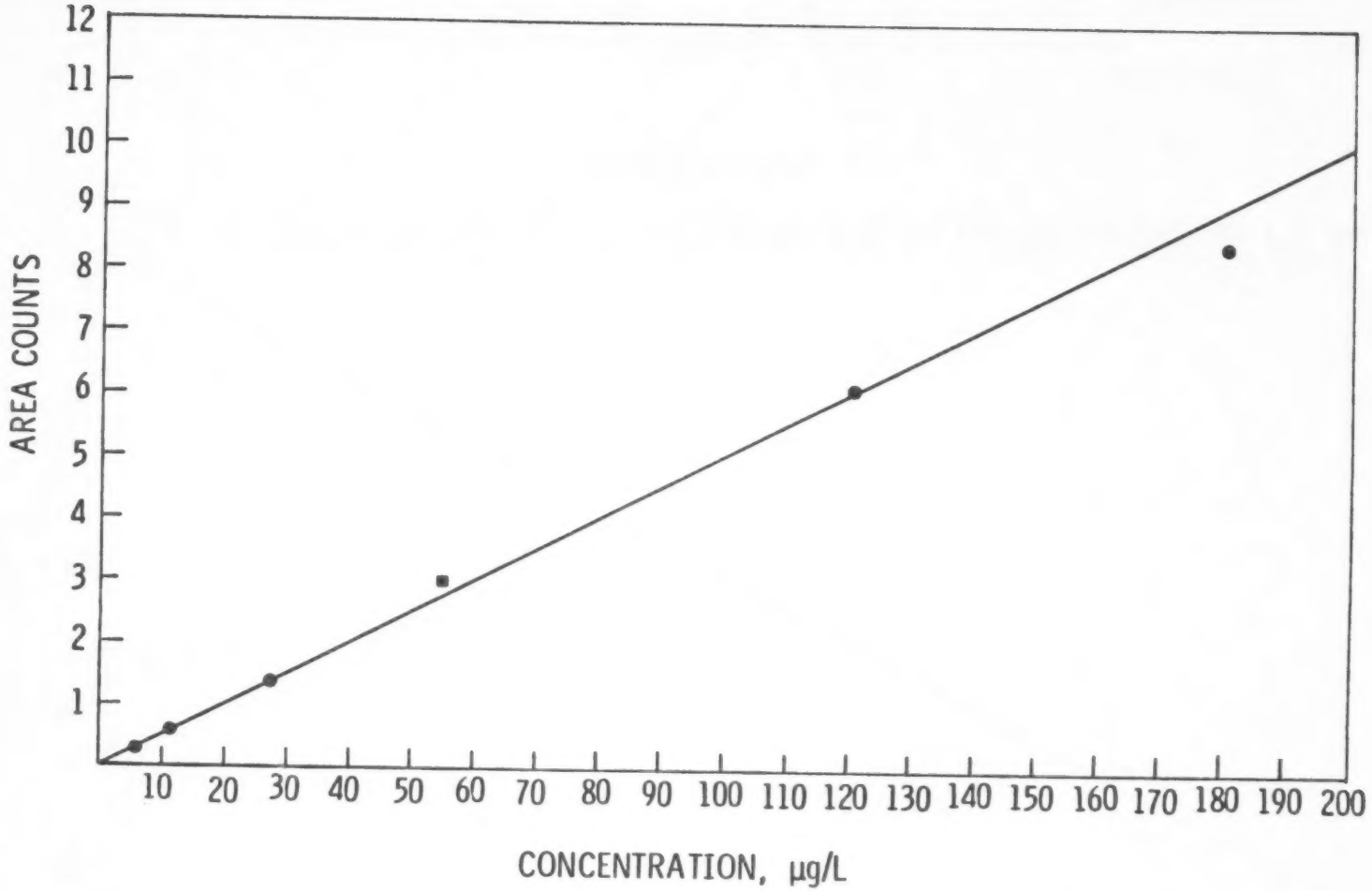


Figure B-1. Calibration curve for chloroform in drinking water by EPA Method 501.2.

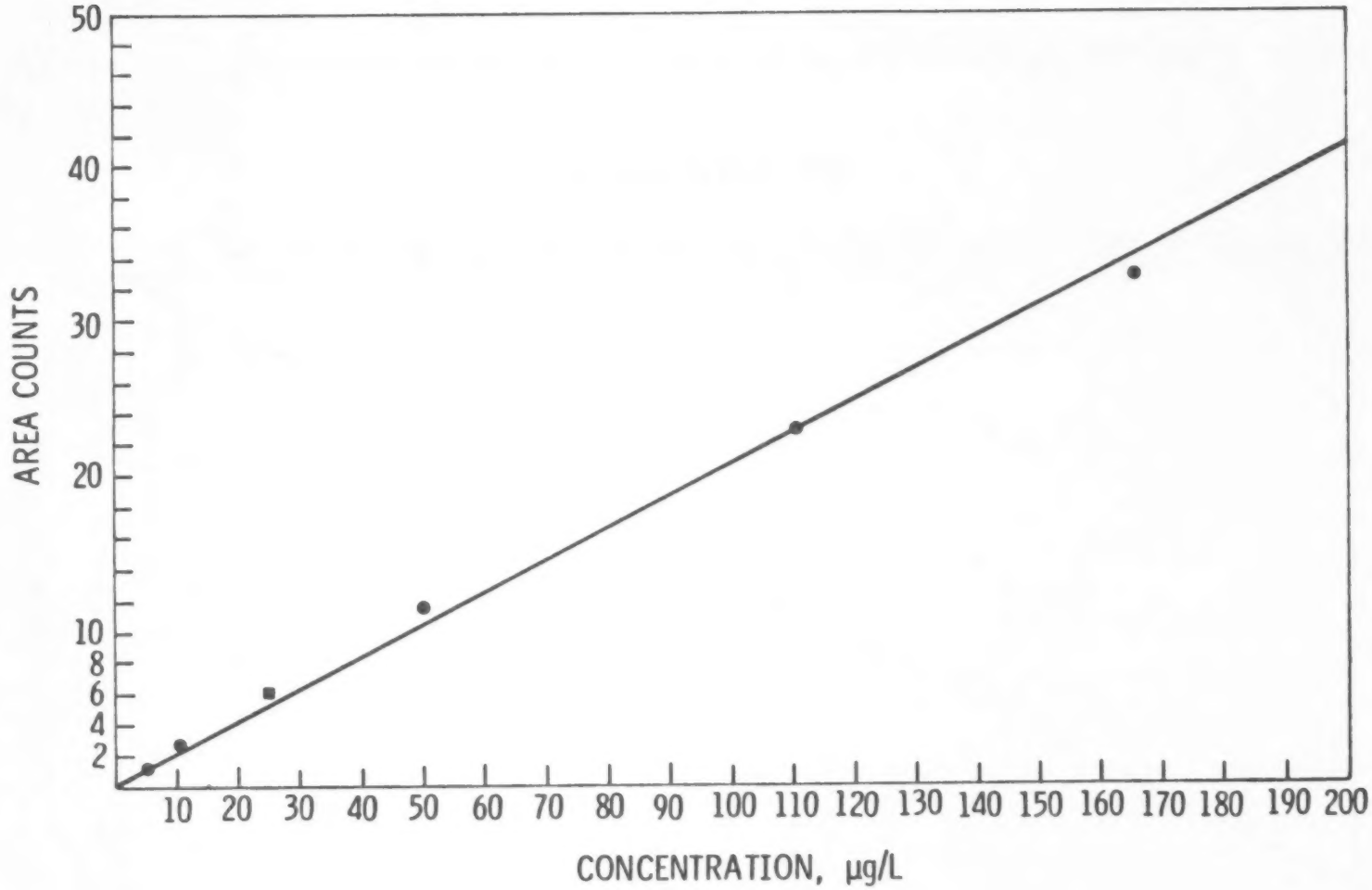


Figure B-2. Calibration curve for bromodichloromethane in drinking water by EPA Method 501.2.

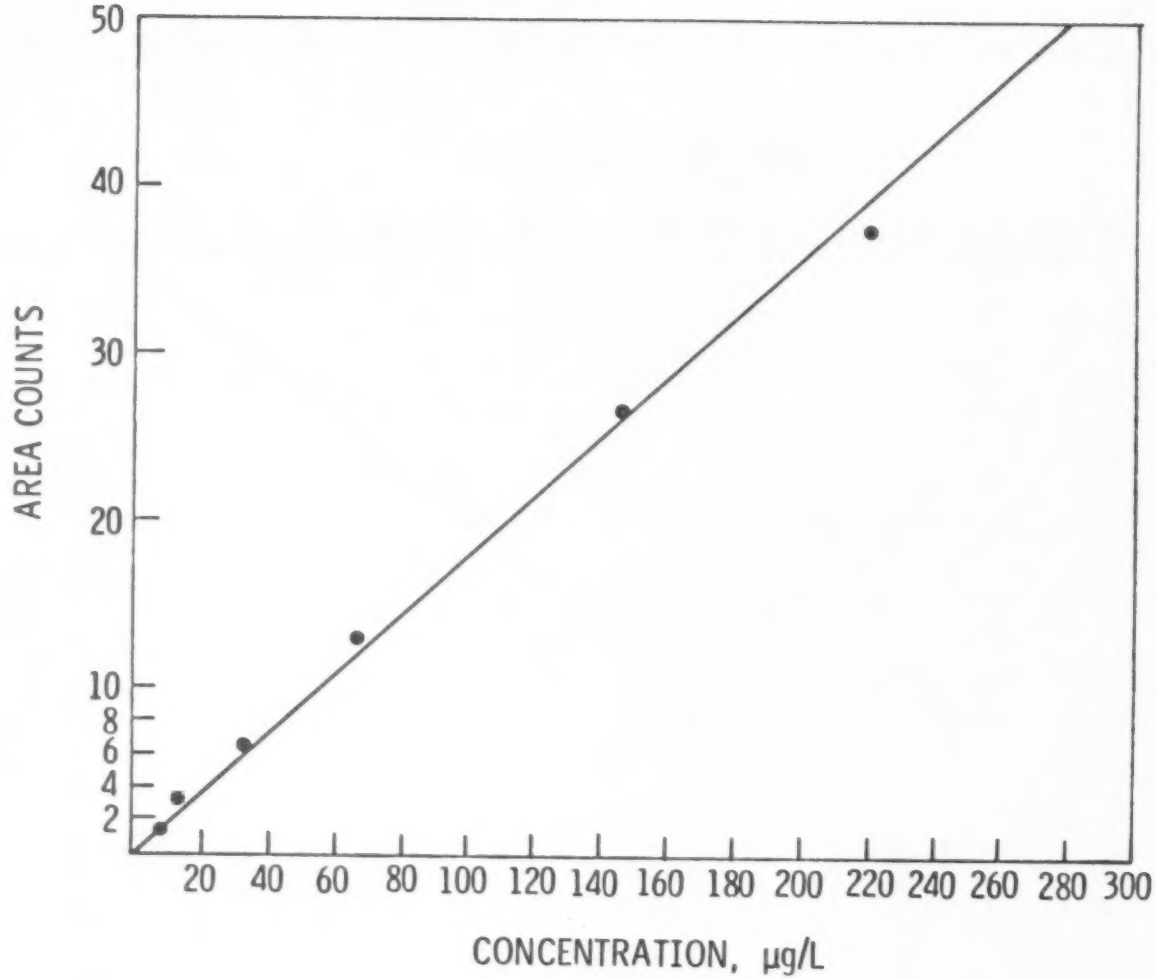


Figure B-3. Calibration curve for chlorodibromomethane in drinking water by EPA Method 501.2.

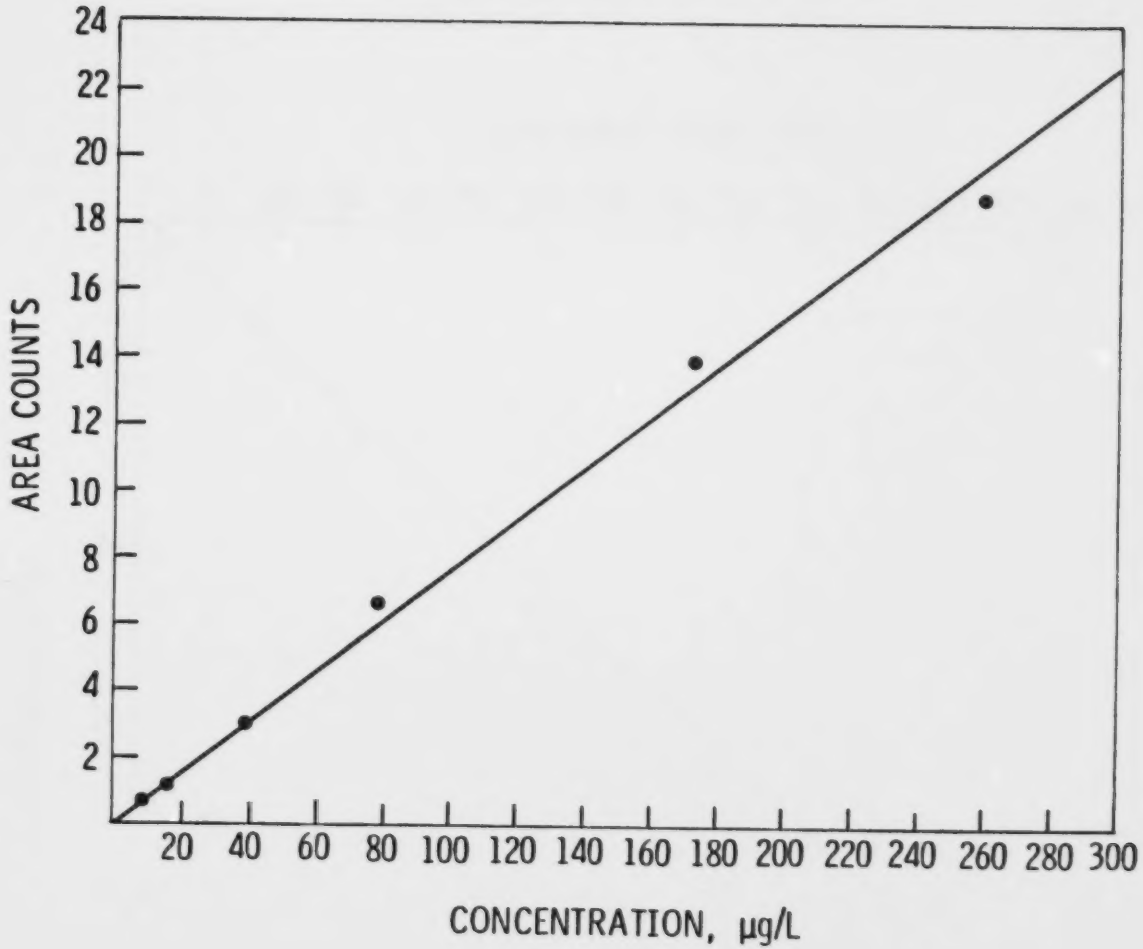


Figure B-4. Calibration curve for bromoform in drinking water by EPA Method 501.2.

APPENDIX C

ANALYSIS OF AMPULS USED IN VALIDATION STUDY OF METHOD 501.2

Concentrated spiking solutions were prepared and sealed in glass ampuls by MRC for the interlaboratory validation study of Method 501.2. The contents of representative ampuls were analyzed, primarily to assure that the more volatile compounds had not been lost during the ampul sealing process. This also would verify that no dilution errors had been made in the preparation of the spiking solutions. Monsanto Research Corporation analyzed the contents of three randomly selected ampuls in triplicate from each concentration for each of the analytes by Method 501.2. The Quality Assurance Branch of EMSL also analyzed the ampuls but used the direct injection GC-MS technique. The data in Table C-1 show close agreement with the true value (T.V) and the analytical value (A.V.).

TABLE C-1. VERIFICATION DATA FOR AMPULS USED IN STUDY OF METHOD 501.2
(ppb)

Ampul number	Chloroform		Bromodichloromethane		Chlorodibromomethane		Bromoform	
	T. V.	A. V.	T. V.	A. V.	T. V.	A. V.	T. V.	A. V.
1	1.76	1.78*	1.76	1.74*	1.76	1.74*	5.99	5.77*
2	2.25	2.27*	2.25	2.27*	2.25	2.27*	7.25	6.82*
3	45.2	43.4	44.8	45.4	44.9	45.6	45.2	45.2
4	55.0	56.2	55.0	60.0	55.0	60.6	55.0	51.6
5	131	127	130	135	131	136	130	132
6	170	179	170	151	174	194	170	191

T. V. = true value.
A. V. = analytical value.
- - - - - - - - - -
The asterisk indicates values generated by EPA; the absence of asterisk indicates values generated by MRC.

APPENDIX D

RAW DATA: METHOD 501.2

TABLE D-1. RAW DATA FOR CHLOROFORM ANALYSIS BY WATER TYPE

EPA METHOD VALIDATION STUDY-MONSANTO METHOD 501.2

LOW YOUDEN PAIR	WATER 1		WATER 2		WATER 1		WATER 2		WATER 1		WATER 2	
	1	2	1	2	3	4	3	4	5	6	5	6
TRUE VALUE UG/L	1.74	2.25	1.74	2.23	45.20	55.09	45.20	55.09	131.00	170.93	131.00	170.30
LABORATORY NUMBER												
11	1.85	2.03	1.95	2.21	43.50	54.39	43.70	53.93	130.00	169.00	133.00	161.00
21	2.88	2.25	1.08	1.23	46.70	57.00	39.60	49.60	124.00	169.00	120.00	163.00
31	0.65	1.73	0.00*	0.00*	41.90	55.90	35.90	50.13	134.00	204.00	170.00	242.00
41	0.42	0.91	0.19	0.21	43.60	55.60	47.50	56.23	127.00	165.00	123.00	153.00
51	1.87	3.07	1.39	2.53	39.70	49.80	41.80	51.50	117.00	154.00	119.00	150.00
61	1.76	2.29	1.70	3.53	41.10	49.90	39.50	44.53	119.00	145.00	105.00	129.00
71	0.68	0.27	0.03*	2.19	36.10	44.60	43.63	65.40	163.00	214.00	260.00*	173.00
81	1.65	1.69	0.03*	0.03*	47.63	61.50	57.10	0.00*	163.00	195.00	99.10	65.10
91	0.57	0.77	0.33	7.30	43.60	50.90	46.50	97.90*	139.00	180.00	177.00	204.00
101	17.20*	13.00*	17.83*	8.29*	77.10*	95.29*	58.60*	74.63*	234.00*	312.00*	254.00*	263.00*
111	2.62	3.03	0.00*	0.23	40.00	42.90	34.30	36.50	115.00	143.00	120.00	139.00
121	9.40*	4.00	8.35*	0.03*	53.20	59.20	46.80	54.00	143.00	178.00	137.00	171.00
131	2.14	2.33	1.44	2.44	42.40	50.80	39.80	46.73	189.00	231.00	188.00	224.00
141	1.12	4.81	0.63	3.13	63.20	70.50	69.40	59.40	162.00	219.00	172.00	227.00
151	1.07	1.39	2.20	4.83	43.10	53.70	47.30	57.70	111.00	146.00	139.00	149.00
161	1.22	1.59	0.29	1.00	31.70	39.53	37.40	40.70	103.00	133.00	110.00	149.00
171	2.20	2.49	1.80	1.73	54.80	48.50	53.40	48.80	103.00	135.00	106.00	134.00
181	2.77	2.90	13.83*	11.99*	49.90	110.00*	79.49*	129.00*	104.00	152.00	569.00*	142.00*
191	0.49	4.28	0.37	9.99	46.40	61.50	45.29	66.93	112.00	164.00	149.00	186.00
201	1.71*	0.47*	1.24*	3.47*	11.29*	13.00*	10.90*	16.10*	30.70*	30.23*	28.50*	44.00*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER*

TABLE D-2. RAW DATA FOR BROMODICHLOROMETHANE ANALYSIS BY WATER TYPE

EPA METHOD VALIDATION STUDY-MONSANTO METHOD 501.2

LOW YOUDEN PAIR	WATER 1		WATER 2		WATER 1		WATER 2		WATER 1		WATER 2	
	1	2	1	2	3	4	3	4	5	6	5	6
TRUE VALUE UG/L	1.76	2.25	1.76	2.25	44.00	55.00	44.00	55.00	130.00	170.00	130.00	170.00
LABORATORY NUMBER												
11	1.70	1.80	1.60	1.99	46.60	51.20	40.70	50.20	120.00	121.00	123.00	115.00
21	1.15	1.37	1.15	1.47	45.00	56.20	44.00	53.60	130.00	132.00	131.00	133.00
31	2.02	2.39	2.45	1.72	52.60	54.20	50.50	49.10	493.00*	1140.00*	1140.00*	2110.00*
41	0.93*	1.06*	1.12	1.29	35.50*	45.80*	35.20	44.10	115.00*	116.00*	113.00	114.00
51	1.65	2.13	1.32	1.67	44.60	51.70	44.50	59.00	127.00	127.00	122.00	122.00
61	1.56	1.94	2.13	2.83	45.30	54.30	44.60	51.30	132.00	124.00	124.00	121.00
71	0.85	1.34	0.99	2.09	33.90	42.30	36.80	36.30	127.00	139.00	144.00	126.00
81	1.67	2.03	0.00*	0.00*	55.10	67.00	56.50*	7.00*	88.50	90.90	94.90*	95.00*
91	1.92	2.48	1.93	3.15	51.70	59.70	53.60	75.20	139.00	129.00	144.00	146.00
101	5.84*	3.79*	5.92	3.46	61.50*	83.20*	56.60	60.50	170.00*	180.00*	196.00	169.00
111	2.90	3.52	0.00*	0.00*	39.10	47.00	40.80*	36.50*	87.30	82.50	98.50*	77.00*
121	6.30*	6.50*	5.00	5.50	45.30	55.70	44.90	53.60	125.00	125.00	115.00	125.00
131	1.85	2.07	1.84	2.12	65.00	73.80	65.00	73.00	137.00	145.00	141.00	145.00
141	0.82	1.60	1.29	2.96	61.60	71.30	69.60	67.90	178.00	179.00	189.00	186.00
151	1.71	2.53	3.56	4.79	44.70	54.80	44.90	55.80	122.00	125.00	129.00	123.00
161	0.91	1.09	1.19	1.23	46.30	60.30	63.60	71.30	183.00	178.00	224.00	217.00
171	2.30	2.80	3.60	4.00	56.10	55.60	56.20	56.80	136.00	138.00	139.00	139.00
181	2.74	2.74	0.00*	0.00*	42.90	92.40*	73.80	104.00*	100.00	133.00	147.00	124.00
191	2.31	3.13	2.45	3.22	55.50	71.60	59.10	73.30	145.00	152.00	163.00	169.00
201	0.76*	1.33*	1.86	0.85	29.60*	29.80*	24.60	34.60	69.30*	55.00*	64.30	75.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE D-3. RAW DATA FOR CHLORODIBROMOMETHANE ANALYSIS BY WATER TYPE

EPA METHOD VALIDATION STUDY-MONSANTO METHOD 501.2

	WATER 1		WATER 2		WATER 1		WATER 2		WATER 1		WATER 2	
LOW YOUDEN PAIR	1	2	1	2	3	4	3	4	5	6	5	6
TRUE VALUE UG/L	1.76	2.25	1.76	2.25	44.93	55.00	44.90	55.00	131.00	174.00	131.00	174.00
LABORATORY NUMBER												
11	1.76	2.07	1.80	2.12	43.20	55.30	43.70	54.23	126.60	166.00	130.00	159.00
21	1.60	1.87	1.71	1.91	42.40	51.10	40.30	42.60	128.00	172.00	128.00	173.00
31	0.84	1.94	2.04	0.24	49.10	58.60	49.60	54.30	214.00	493.00*	175.00*	410.00*
41	1.71	1.77	1.60	1.83	53.00	66.20	52.30	66.50	150.00	208.00	197.00	205.00
51	1.67	2.15	1.86	2.39	46.40	54.60	46.50	56.30	122.30	170.00	174.00	171.00
61	1.38	1.69	1.45	1.76	46.00	55.50	45.30	52.67	138.00	166.00	131.30	155.00
71	0.80	1.24	1.17	2.29	35.20	43.10	39.90	46.70	156.00	221.00	153.00	193.00
81	1.43	1.97	0.00*	0.00*	45.00	59.50	43.60*	14.10*	144.00	170.00	71.35*	55.10*
91	1.96	2.36	1.69	2.17	54.00	62.20	54.70	76.53	146.00	185.00	196.00	196.00
101	4.24*	3.25*	3.57*	2.35*	58.53*	79.23*	57.55*	59.40*	183.00*	248.00*	196.00*	222.00*
111	2.04	3.17	0.00*	0.13*	40.80	49.43	41.65*	36.00*	85.50	93.00	97.10*	97.13*
121	3.63	3.90	3.60	3.70	46.50	55.19	43.78	53.30	129.00	167.00	126.00	163.00
131	1.81	1.94	1.81	2.03	36.50	44.00	35.50	43.17	119.00	147.00	122.00	143.00
141	0.64	1.00	1.76	1.09	49.60	57.90	50.80	52.53	145.00	196.30	159.30	207.00
151	1.57	2.23	1.73	2.17	42.60	52.33	43.20	54.10	116.00	165.00	123.00	163.00
161	1.08	1.26	1.31	1.51	43.60	57.20	56.40	65.30	478.00	242.00	717.00*	288.60*
171	2.93	3.50	3.00	3.70	49.00	59.60	47.80	49.00	114.00	153.00	119.70	155.00
181	2.74	2.81	0.89	1.12	39.90	86.50*	70.30*	94.60*	112.00	137.00	117.00	139.00
191	2.24	2.94	2.39*	2.28*	56.40	71.70	98.80*	74.10*	156.00	202.00	169.83*	220.00*
201	1.17*	1.8?*	2.50	1.??	39.00*	45.80*	37.20	53.00	109.00*	109.00*	99.50	149.00

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE D-4. RAW DATA FOR BROMOFORM ANALYSIS BY WATER TYPE

LOW YOUDEN PAIR	WATER 1		WATER 2		WATER 1		WATER 2		WATER 1		WATER 2	
	1	2	1	2	3	4	3	4	5	6	5	6
TRUE VALUE UG/L	5.99	7.25	5.93	7.75	45.20	55.00	49.20	55.00	130.00	170.00	130.00	170.00
LABORATORY NUMBER												
11	4.47	5.31	4.90	5.33	43.00	53.90	49.20	52.50	127.00	165.00	130.00	159.00
21	4.47	4.39	3.95	4.65	44.73	56.60	42.50	51.60	127.00	166.00	124.00	164.00
31	3.06*	3.46*	3.06*	3.62*	38.60*	43.60*	39.30*	33.70*	64.80*	99.50*	99.50*	96.10*
41	3.90	4.09	4.10	4.72	40.30	49.90	49.30	50.33	126.00	162.00	121.00	152.00
51	4.09	4.69	4.98	4.86	41.30	51.20	41.00	52.20	*112.00	156.00	119.00	160.00
61	4.73	5.09	5.66	5.67	47.33	55.10	47.10	52.73	139.00	165.00	134.00	171.00
71	3.39	3.39	0.00*	0.00*	36.33	44.20	36.70	42.60	123.00	151.00	115.00	155.00
81	2.32	4.49	3.29*	3.99*	38.10	46.33	37.10*	19.20*	114.00	148.00	94.50*	62.20*
91	5.09	5.89	4.29	5.33	55.20	63.70	55.93	75.63	146.00	183.00	154.00	196.00
101	9.12*	6.87*	7.18*	5.73*	57.40*	76.00*	49.60*	89.50*	198.00*	266.00*	139.00*	237.00*
111	2.93	4.80	1.03*	2.59	42.40	49.20	45.70	43.70	96.50	129.00	96.70	122.00
121	0.00*	0.00*	0.00*	3.12	54.80	66.90	53.40	66.50	175.00	226.00	143.00	232.00
131	4.07	4.19	4.07	4.36	41.10	66.40	41.10	45.90	123.00	158.00	133.00	158.00
141	3.09	4.31	3.84	3.81	48.50	58.60	49.40	53.20	144.00	185.00	145.00	191.00
151	5.47	6.37	5.70	6.33	48.10	59.90	47.90	62.00	137.00	182.00	145.00	178.33
161	2.91	4.51	4.04	3.45	39.83	51.30	42.90	43.73	134.00	174.00	141.00	195.00
171	4.20	4.70	5.49	5.83	60.60	58.70	60.10	60.60	143.00	192.00	151.00	196.00
181	7.98*	7.53*	7.66*	8.00*	47.20	102.00*	53.80*	108.00*	101.00	167.00	220.00*	160.33*
191	7.05*	8.05*	7.13*	9.18*	37.30*	71.80*	60.23*	75.50*	159.00*	200.00*	147.00*	217.00*
201	3.84	5.11	4.91	4.85	36.50	43.00	35.00	48.60	105.00	105.00	95.10	144.00

* = REJECTED

WATER LEGEND

1 = DISTILLED WATER
2 = TAP WATER

TABLE D-5. BLANK VALUES FOR VALIDATION ANALYSES

Laboratory	Distilled water				Tap water			
	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform	Chloroform	Bromodichloromethane	Chlorodibromomethane	Bromoform
1	0	0	0	0	0	0	0	0
2	0	0	0	0	34.5	4.82	0.73	0
3	<0.02	<0.02	<0.02	<0.02	62.0	1.00	<0.02	<0.08
4	8.90	4.52	.77	0	17.3	4.29	1.49	0
5	0.03	0	0	0.21	18.1 (55.0)[a]	12.7 (16.8)	6.10 (7.40)	0.24 (0.34)
6	0	0	0	0	39.1	4.23	0	0
7	<0.2	<0.2	<0.2	<0.5	1.0	4.4	6.1	12.9
8	0.79	0	0	0	52.6	13.9	3.22	0
9	0	0	0	0	81.3 (74.1, 71.6)[b]	32.0 (31.5, 33.7)	10.6 (9.30, 12.4)	1.89 (1.70, 2.4)
10	0	0	0	0	68.9	7.66	0.14	0
11	0	0	0	0	12.3	14.6	17.5	7.28
12	0.96	0	0	0	34.7	9.54	0.37	0
13	0	0	0	0	0	0	0	0
14	0.37	0.09	0.15	0.22	15.5	5.83	1.42	0.11
15	0	0	0	0	34.6	2.42	0	0
16	0.10	0.05	0.18	0.09	12.0	14.5	8.12	0.35
17	0	0	0	0	0	0	0	0
18	0.45	0.22	0	0	27.1	4.50	0.45	0
19	0	0	0	0	0.64	0	0	0
20	1.24	<0.5	<0.5	<0.5	7.90	0.70	<0.5	<0.5

[a]Values in parentheses for ampuls 5 and 6.

[b]First value in paranthesis for ampuls 3 and 4, second value in parenthesis for ampuls 5 and 6.